Notice of RCRA Class 1 Permit Modification in Accordance with 20.4.1.900 NMAC (incorporating 40 CFR Part 270)

Waste Isolation Pilot Plant
Carlsbad, New Mexico

November 13, 2000

Notice of RCRA Class 1 Permit Modification in Accordance with 20.4.1.900 NMAC (incorporating 40 CFR Part 270)

Consistent with requirements of 20.4.1.900 New Mexico Administrative Code (NMAC) (hereafter referred to as Part 270 or Section 270.XX) the U.S. Department of Energy, Carlsbad Area Office is submitting to the New Mexico Environment Department (NMED) a notice of Class 1 modifications to the Hazardous Waste Facility Permit (NM4890139088-TSDF) for the Waste Isolation Pilot Plant (WIPP). Specifically, this information is provided to comply with the requirements of Section 270.42(a)(1).

The modifications are listed in Table 1. Listed information includes a reference to the applicable section of the permit, a brief description of each item, and the class of the item, as identified in Appendix I to Section 270.42. The relevant permit modification category, as identified in Appendix I, is provided as well. A more complete description of the Class 1 modifications are provided in Attachment A. Several of these modifications are the result of discussions with the NMED regarding Class 1 modifications that were previously submitted. The NMED requested that changes be made in several of the previous modifications to clarify the change or to resolve other difficulties identified by the NMED. Each is discussed separately in Attachment A.

The identified changes do not substantially alter the permit conditions or reduce the capacity of the facility to protect human health or the environment and the modified permit is no less stringent than the current permit.

Table 1. Class 1 Hazardous Waste Facility Permit Modification

No.	Affected Permit Section	Item	Category	Attachment 1 Page #
1	a. Attach. B1	Drum Age Criteria	A..3	A-1

Attachment A

Descriptions of the Hazardous Waste Facility Class 1 Permit Modification

Item 1

Description:

Establish the drum age criteria (DAC) necessary for taking a representative headspace gas sample based on packaging configuration groups.

Basis:

In responses to comments on both the draft Permit and the revised draft Permit, the NMED established three points regarding the DAC values:

1. Drum age must assure headspace gas has reached 90% steady-state to preclude the necessity to collect samples from innermost layers of confinement.

2. Additional studies and experimental studies are required to justify alternative values.

3. Standardized values retain simplicity within the Permit.

These additional criteria are based on analysis and studies of specific packaging configurations anticipated to be typical of mixed TRU waste packaging. In addition, the results are applied simply through the addition of look-up tables to the Permit.

Section B1-1a of the Permit establishes that a DAC must be met "to ensure that the drum contents have reached 90 percent of steady state concentration within each layer of confinement." The section also establishes a DAC for S5000 (Debris) waste as a minimum of 142 days after packaging and a DAC for S3000 (Homogeneous solids) and S4000 (Soil/gravel) waste as a minimum of 225 days after packaging. These DACs only considered the time necessary to meet the 90 percent of steady state concentration criterion for a conservative bounding packaging configuration for each of the summary category groups and did not consider other packaging configurations that occur in transuranic (TRU) waste drums.

This permit modification establishes additional criteria in the form of packaging configuration DACs to ensure that DACs for packaging configurations other than the bounding configurations are established based on the 90 percent of steady state criterion. This modification also includes packaging configuration DACs for drums containing pipe components, which were not considered in the original analysis used to establish the DACs.

The packaging configuration DACs proposed in this modification were developed using the same model and calculation methodology as that used in developing the DACs using the bounding packaging configuration. The proposed packaging configuration DACs include the same 142 and 225 day DACs for the packaging configuration used in the original bounding analysis and does not reduce any of the requirements for meeting the DAC to ensure 90 percent of steady state concentration within each layer of confinement has been reached. Therefore this modification presents additional criteria that must be met based on the individual packaging configurations using a functionally equivalent methodology to ensure 90 percent of steady state concentrations are established.

In addition, this modification proposes to eliminate an inconsistency within the permit when using the term “unvented rigid container greater than 4 liters.” The way this term is used implies that the drum liner is considered an unvented container greater than 4 liters, which is inconsistent with the referenced INEEL report (Lockheed 1995). To address this inconsistency, the permit modification establishes three different sampling scenarios for containers subject to headspace gas sampling.

The Permit also contains language in Sections B1-1a(3)(i), B1-1a(3)(ii), and B1-1a(3)(iii) that states that a representative sample cannot be collected until the poly-liner has been vented to the drum. This is only applicable to samples that are taken between the drum lid and the liner. Samples that are taken from within the drum liner are representative if the appropriate DAC has been met. Therefore, the language in this section has been modified to address this inconsistency as well.

Discussion:

Section B1-1a of the Permit establishes that the DAC must be met “to ensure that the drum contents have reached 90 percent of steady state concentration within each layer of confinement.” The section also establishes the DACs for S5000 (Debris) waste as a minimum of 142 days after packaging and for S3000 (Homogeneous solids) and S4000 (Soil/gravel) waste as a minimum of 225 days after packaging. These values are based on the results of the Lockheed (1995) report. This document describes the model and methodology used to establish the 142 and 225 day DACs. This document based the final DACs on a conservative bounding packaging configuration and sampling time that would cause the DAC to be the longest. This approach was used to make the process of determining the DAC to be as simple as possible.

The DAC is a variable with a unique value for each packaging configuration. The DAC values in the Permit of 142 days and 225 days were based on the bounding packaging configurations (i.e. those representing the highest resistance to VOC transport and thus longest DACs) and toluene was used as the bounding VOC based on its prevalence, as reported by DOE sites, and slow transport characteristics. A computer program was used to calculate the DAC values for the bounding packaging configurations. The computer program represents a VOC transport model that calculates the transient VOC gas-phase concentrations throughout a waste drum. The model consists of a series of material balance equations describing the transient VOC transport across layers of confinement in a container. The primary mechanisms for gas transport across a confinement layer are permeation across a polymeric layer, diffusion through air across an opening in the layer, and diffusion through a filter vent in the case of a drum filter or filtered bag. One or all of these mechanisms of transport may be operating depending on the characteristics of the confinement layer. The governing equations for the model are presented in Lockheed (1995) and BWXT (2000)[1]. The model was validated with actual drum VOC testing data as documented in Lockheed (1995).

[1] BWXT (2000) is included as Attachment B.

There are three different sampling scenarios that are applicable to containers subject to headspace gas sampling. These scenarios are:

a. Drums that are unvented and are sampled under the rigid liner (if present) at the time of venting.

b. Drums that have been packaged for a specified period of time sufficient to achieve equilibrium conditions (i.e., met the DAC for Scenario 1 drums) and then are vented, but not sampled at the time of venting.

c. Containers (i.e., drums, SWBs, and pipe components) that are initially packaged in a vented condition and sampled in the container headspace.

In addition to the bounding packaging configuration, the DACs that are established in the Permit are based on the bounding scenario. Because drums that fall under Scenario 1 have been packaged for a long period of time, the DACs for drums under Scenario 1 were calculated based on the most restrictive packaging configuration, which is 6 layers of confinement for S3000/S4000 waste and 2 layers of packaging for S5000 waste. Table 1 contains the matrix of DACs that are applicable to containers that are covered under Scenario 1. The statements in B1-1a(3)(i), B1-1a(3)(ii), and B1-1a(3)(iii) that a representative sample cannot be collected unless the drum liner is vented do not apply to samples taken for Scenario 1. This is because meeting the Scenario 1 DAC ensures that a representative sample may be collected, provided it is collected from within the drum liner.

Scenario 2 is for drums that are not sampled at the time of venting. Because a Scenario 2 drum has already reached equilibrium conditions prior to venting, the initial condition used to determine the DAC applicable after venting is based on equilibrium conditions rather than the zero concentration conditions of Scenario 3. However, if an unvented drum has not reached equilibrium (i.e., not met the Scenario 1 DAC) prior to venting, the drum must be classified under Scenario 3. Table 2 contains the Scenario 2 DAC matrix.

To evaluate the development of DACs for Scenario 3, a survey of U.S. Department of Energy (DOE) sites expected to generate and package CH-TRU waste in the future and a review of TRUCON codes was conducted. This review indicated that the packaging configurations can be summarized under a number of common configurations (BWXT 2000). These common configurations were divided into the two major categories: (1) packaging configurations of containers belonging to summary categories S3000 (Homogenous solids) and S4000 (Soil/gravel), and (2) packaging configurations of containers belonging to summary category S5000 (Debris waste).

Table 3 lists the packaging configurations applicable to Scenario 3 that were considered, with the bounding configuration (i.e., the configuration that results in the longest DAC) identified. In addition to the drum packaging configurations, packaging configurations for the pipe component and standard waste box (SWB) were evaluated. The pipe component is a metal pipe with a filtered lid that contains waste and conceptually is similar to a small drum in its configuration. The pipe component is then overpacked in a drum for shipment and disposal. Similarly to other overpacked containers (e.g., drums inside of a standard waste box), the headspace gas sampling for pipe components is focused on the headspace of the pipe component, which then must be conservatively assigned to the overpacked container (in this case the drum).

Therefore, the pipe component was modeled like a drum and a DAC established for sampling the pipe component. Therefore, after the DAC is met, the sample must be taken from the pipe component headspace and conservatively assigned to the overpack drum.

The VOC transport model computer program was used to generate a matrix of packaging-specific DAC values for Scenario 3 (Tables 4 and 5). The bounding DAC value of 225 days (summary categories S3000 (Homogenous solids) and S4000 (Soil/gravel)) is part of the matrix, because the original bounding configurations used remain bounding for that packaging configuration. The DAC of 142 days (summary category S5000 (Debris waste) with 5 layers of confinement) has been updated to 148 days because 6 layers of confinement represent the bounding case for packaging configuration 3; however, the 142 day DAC is valid as long as the packaging configuration does not exceed a total of 5 layers of confinement.

To obtain the appropriate DAC value of a container, the sampling scenario is identified and then, if applicable, the actual container packaging configuration is assigned to one of the packaging configuration groups. The DAC for the container is then located on the applicable sampling scenario matrix by looking up the entry that corresponds to the appropriate summary category group, bounding packaging configuration, filter diffusivity, and rigid drum liner hole size of the container being evaluated.

The permit currently implies that if a container has met the DAC in an unvented condition and the headspace gas sample is not taken at the time of venting, the DAC must be re-met prior to sampling. This implication comes from the reference to unvented rigid containers greater than 4 liters. It can be interpreted that the reference to unvented sealed rigid containers greater than 4 liters includes the drum liner. This is not the case. The DAC reports indicate that if the drum has met the Scenario 1 DAC in an unvented condition, a specific waiting period (i.e., Scenario 2 DAC) is needed for re-equilibration of the headspace gas after venting the drum liner if a sample is not taken at the time of venting. This contradicts the implication in the permit regarding 4 liter sealed containers. Therefore, the language in this permit modification relative to sampling Scenario 2 revises the permit to eliminate this potential inconsistency.

If additional packaging configurations are identified at a later date, a Class 1 Permit modification will be submitted to incorporate an appropriate DAC. Sites are encouraged to use packaging configurations that have a DAC established whenever possible.

References

BWXT, 2000, Determination of Drum Age Criteria and Prediction Factors Based on Packaging Configurations, INEEL/EXT-2000-01207, October 2000, Liekhus, K.J., S.M. Djordjevic, M. Devarakonda, and M.J. Connolly, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho.

Lockheed Idaho Technologies Company, 1995, Position for Determining Gas Phase Volatile Organic Compound Concentrations in Transuranic Waste Containers, INEL-95/0109/Revision 1, M.J. Connolly, et. al.

Table 1. Scenario 1 DAC Matrix

Summary Category Group	DAC (days)
S3000/S4000	127
S5000	53

Table 2. Scenario 2 DAC Matrix

	Summary Category Group S3000/S4000				Summary Category Group S5000			
Filter H_2 Diffusivity	**Liner Lid Opening Diameter**				**Liner Lid Opening Diameter (in)**			
(mol/s/mol fraction)	0.30	0.375	0.75	1.0	0.30	0.375	0.75	1.0
1.9×10^{-6}	36	30	23	22	29	22	13	12
3.7×10^{-6}	30	25	19	18	25	20	12	11
3.7×10^{-5}	13	11	11	11	7	6	6	4

Table 3
Scenario 3 Packaging Configurations

Packaging Configuration Group	Covered Packaging Configurations
Packaging Configuration 1, drums	• No layers of confinement, filtered inner lid • No inner bags, no liner bags (bounding case)
Packaging Configuration 2, drums	• 1 inner bag • 1 filtered inner bag • 1 liner bag • 1 filtered liner bag • 1 inner bag, 1 liner bag • 1 filtered inner bag, 1 filtered liner bag • 2 inner bags • 2 filtered inner bags • 2 inner bags, 1 liner bag • 2 filtered inner bags, 1 filtered liner bag • 3 inner bags • 3 filtered inner bags • 3 filtered inner bags, 1 filtered liner bag • 3 inner bags, 1 liner bag (bounding case)
Packaging Configuration 3, drums	• 2 liner bags • 2 filtered liner bags • 1 inner bag, 2 liner bags • 1 filtered inner bag, 2 filtered liner bags • 2 inner bags, 2 liner bags • 2 filtered inner bags, 2 filtered liner bags • 3 filtered inner bags, 2 filtered liner bags • 4 inner bags • 3 inner bags, 2 liner bags • 4 inner bags, 2 liner bags (bounding case)
Packaging Configuration 4, pipe components	• No layers of confinement inside a pipe component • 1 filtered inner bag, 1 filtered metal can inside a pipe component • 2 inner bags inside a pipe component • 2 filtered inner bags inside a pipe component • 2 filtered inner bags, 1 filtered metal can inside a pipe component • 2 inner bags, 1 filtered metal can inside a pipe component (bounding case)
Packaging Configuration 5, Standard Waste Box	• No layers of confinement • 1 SWB liner bag (bounding case)
Packaging Configuration 6, Standard Waste Box	• any combination of inner and/or liner bags that is less than or equal to 6 • 5 inner bags, 1 SWB liner bag (bounding case)

Table 4
Scenario 3 Drum Age Criteria (in days) Matrix for S3000 and S4000 Waste by Packaging Configuration Group

Packaging Configuration 1						
Filter H_2 Diffusivity (mol/s/mol fraction)	Liner Lid Hole Size				No Liner Lid	No Liner
	0.3-inch Diameter Hole	0.375-inch Diameter Hole	0.75-inch Diameter Hole	1-inch Diameter Hole		
1.9×10^{-6}	131	95	37	24	4	4
3.7×10^{-6}	111	85	36	24	4	4
3.7×10^{-5}	28	28	23	19	4	4

Packaging Configuration 2						
Filter H_2 Diffusivity (mol/s/mol fraction)	Liner Lid Hole Size				No Liner Lid	No Liner
	0.3-inch Diameter Hole	0.375-inch Diameter Hole	0.75-inch Diameter Hole	1-inch Diameter Hole		
1.9×10^{-6}	213	175	108	92	56	18
3.7×10^{-6}	188	161	105	90	56	17
3.7×10^{-5}	80	80	75	71	49	10

Packaging Configuration 3						
Filter H_2 Diffusivity (mol/s/mol fraction)	Liner Lid Hole Size				No Liner Lid	No Liner
	0.3-inch Diameter Hole	0.375-inch Diameter Hole	0.75-inch Diameter Hole	1-inch Diameter Hole		
1.9×10^{-6}	283	243	171	154	107	34
3.7×10^{-6}	253	225	166	151	106	31
3.7×10^{-5}	121	121	115	110	84	13

Packaging Configuration 4	
Filter H_2 Diffusivity (mol/s/mol fraction)	Headspace Sample Taken Inside Pipe Component
$> 1.9 \times 10^{-6}$	152

Packaging Configuration 5	
Filter H_2 Diffusivity [a] (mol/s/mol fraction)	**Headspace Sample Taken Inside SWB**
> 7.4 x 10^{-6}	15

Packaging Configuration 6	
Filter H_2 Diffusivity [a] (mol/s/mol fraction)	**Headspace Sample Taken Inside SWB**
> 7.4 x 10^{-6}	56

[a] The filter H_2 diffusivity for SWBs is the sum of the diffusivities for all of the filters on the SWB because an SWB has more than 1 filter.

Table 5
Scenario 3 Drum Age Criteria (in days) Matrix for S5000 Waste
by Packaging Configuration Group

Packaging Configuration 1						
	Liner Lid Hole Size					
Filter H_2 Diffusivity (mol/s/mol fraction)	0.3-inch Diameter Hole	0.375-inch Diameter Hole	0.75-inch Diameter Hole	1-inch Diameter Hole	No Liner Lid	No Liner
1.9×10^{-6}	131	95	37	24	4	4
3.7×10^{-6}	111	85	36	24	4	4
3.7×10^{-5}	28	28	23	19	4	4

Packaging Configuration 2						
	Liner Lid Hole Size					
Filter H_2 Diffusivity (mol/s/mol fraction)	0.3-inch Diameter Hole	0.375-inch Diameter Hole	0.75-inch Diameter Hole	1-inch Diameter Hole	No Liner Lid	No Liner
1.9×10^{-6}	175	138	75	60	30	11
3.7×10^{-6}	152	126	73	59	30	11
3.7×10^{-5}	58	57	52	47	28	8

Packaging Configuration 3						
	Liner Lid Hole Size					
Filter H_2 Diffusivity (mol/s/mol fraction)	0.3-inch Diameter Hole	0.375-inch Diameter Hole	0.75-inch Diameter Hole	1-inch Diameter Hole	No Liner Lid	No Liner
1.9×10^{-6}	197	161	96	80	46	16
3.7×10^{-6}	175	148[a]	93	79	46	16
3.7×10^{-5}	72	72	67	62	42	10

Packaging Configuration 4	
Filter H_2 Diffusivity (mol/s/mol fraction)	Headspace Sample Taken Inside Pipe Component
$> 1.9 \times 10^{-6}$	152

Packaging Configuration 5	
Filter H_2 Diffusivity [b] (mol/s/mol fraction)	**Headspace Sample Taken Inside SWB**
> 7.4×10^{-6}	15

Packaging Configuration 6	
Filter H_2 Diffusivity [b] (mol/s/mol fraction)	**Headspace Sample Taken Inside SWB**
> 7.4×10^{-6}	56

[a] A DAC of 142 days can be used for this case provided the packaging configuration does not exceed a total of 5 layers of confinement.

[b] The filter H_2 diffusivity for SWBs is the sum of the diffusivities for all of the filters on the SWB because an SWB has more than 1 filter.

Revised Permit Text:

a. 1. Attachment B1

List of Tables

a. 2. Attachment B1-1a

The Permittees shall require all headspace-gas sampling be performed in an appropriate radiation containment area on waste containers that are in compliance with the container equilibrium requirements (i.e. 72 hours at 18E C or higher). All waste containers or randomly selected containers from waste streams that meet the conditions for reduced headspace gas sampling listed in Section B-3a(1) designated as summary category S5000 (Debris waste) shall be categorized under one of the sampling scenarios shown in Table B1-5. If the container is categorized under Scenario 1 or 2, the applicable drum age criteria (DAC) from Tables B1-6 and B1-7 must be met prior to headspace gas sampling. Containers categorized under Scenario 3 must be placed into one of the packaging configuration groups listed in Table B1-8. If a container is designated as packaging configuration group 4 (i.e., a pipe component), the headspace gas sample must be taken from the pipe component headspace. Each of the Scenario 3 containers shall be sampled for headspace gas after waiting the DAC in Table B1-9 based on its packaging configuration (note: packaging configurations 4, 5, and 6 are not summary category group dependent) ~~a minimum of 142 days after packaging~~. All waste containers or randomly selected containers from waste streams that meet the conditions for reduced headspace gas sampling listed in Section B-3a(1) designated as summary categories S3000 (Homogenous solids) and S4000 (Soil/gravel) shall be categorized under one of the sampling scenarios shown in Table B1-5. If the container is categorized under Scenario 1 or 2, the applicable drum age criteria (DAC) from Tables B1-6 and B1-7 must be met prior to headspace gas sampling. Containers categorized under Scenario 3 must be placed into one of the packaging configuration groups listed in Table B1-8. If a container is designated as packaging configuration group 4 (i.e., a pipe component), the headspace gas sample must be taken from the pipe component headspace. Each of the Scenario 3 containers shall be sampled after waiting the DAC in Table B1-10 based on its packaging configuration (note: packaging configurations 4, 5, and 6 are not summary category group dependent) ~~a minimum of 225 days after packaging~~. These ~~This~~ drum age criteria are ~~is~~ to ensure that the ~~drum~~ container contents have reached 90 percent of steady state concentration within each layer of confinement (Lockheed, 1995, BWXT 2000). The equilibrium time and drum age of all containers from which a headspace gas sample is collected will be documented in headspace gas sampling documents. All waste containers with unvented rigid containers greater than 4 liters, except for drum liners and/or Waste Material Type II.2 packaged in a metal container, shall be subject to innermost layer of containment sampling or shall be vented ~~prior to initiating drum age and equilibrium criteria~~. The configuration of the containment area and remote-handling equipment at each sampling facility are expected to differ. Headspace-gas samples will be analyzed for the analytes listed in Table B3-2 of Permit Attachment B3.

a. 3. Attachment B1-1a(3)(i)

- The lid of the drum's 90-mil poly liner shall contain a hole for venting to the drum. A representative sample cannot be collected until the poly-liner has been vented to the drum, unless the DAC for Scenario 1 is met and the sample is collected from inside the drum liner. If headspace-gas samples are collected from outside the drum liner prior to venting the 90-mil poly liner, the sample is not acceptable and a nonconformance report shall be prepared, submitted, and resolved. Nonconformance procedures are outlined in Permit Attachment B3.

a. 4. Attachment B1-1a(3)(ii)

- The lid of the drum's 90-mil poly liner shall contain a hole for venting to the drum. A representative sample cannot be collected until the poly-liner has been vented to the drum, unless the DAC for Scenario 1 is met and the sample is collected from inside the drum liner. If headspace-gas samples are collected from outside the drum liner prior to venting the 90-mil poly liner, the sample is not acceptable and a nonconformance report shall be prepared, submitted, and resolved. Nonconformance procedures are outlined in Permit Attachment B3.

a. 5. Attachment B1-1a(3)(iii)

- The lid of the drum's 90-mil poly liner shall contain a hole for venting to the drum. A representative sample cannot be collected until the poly-liner has been vented to the drum, unless the DAC for Scenario 1 is met and the sample is collected from inside the drum liner. If headspace-gas samples are collected from outside the drum liner prior to venting the 90-mil poly liner, the sample is not acceptable and a nonconformance report shall be prepared, submitted, and resolved. Nonconformance procedures are outlined in Permit Attachment B3.

a. 6. Attachment B1-6

BWXT, 2000, Determination of Drum Age Criteria and Prediction Factors Based on Packaging Configurations, INEEL/EXT-2000-01207, October 2000, Liekhus, K.J., S.M. Djordjevic, M. Devarakonda, and M.J. Connolly, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho.

a. 7. Attachment B1, Table B1-5

TABLE B1-5

HEADSPACE GAS DRUM AGE CRITERIA SAMPLING SCENARIOS

Scenario	Description
1	Drums that are unvented and are sampled under the rigid liner (if present) at the time of venting.
2	Drums that have been packaged for a specified period of time sufficient to achieve equilibrium conditions (i.e., met the DAC for Scenario 1 drums) and then are vented, but not sampled at the time of venting.
3	Containers (i.e., drums, SWBs, and pipe components) that are initially packaged in a vented condition and sampled in the container headspace.

a. 8. Attachment B1, Table B1-6

TABLE B1-6

SCENARIO 1 DRUM AGE CRITERIA (in days) MATRIX

Summary Category Group	DAC (days)
S3000/S4000	127
S5000	53

a. 9. Attachment B1, Table B1-7

TABLE B1-7

SCENARIO 2 DRUM AGE CRITERIA (in days) MATRIX

	Summary Category Group S3000/S4000				Summary Category Group S5000			
Filter H_2 Diffusivity	**Liner Lid Opening Diameter**				**Liner Lid Opening Diameter (in)**			
(mol/s/mol fraction)	0.30	0.375	0.75	1.0	0.30	0.375	0.75	1.0
1.9×10^{-6}	36	30	23	22	29	22	13	12
3.7×10^{-6}	30	25	19	18	25	20	12	11
3.7×10^{-5}	13	11	11	11	7	6	6	4

a. 10. Attachment B1, Table B1-8

TABLE B1-8
SCENARIO 3 PACKAGING CONFIGURATIONS

Packaging Configuration Group	**Covered Packaging Configurations**
Packaging Configuration 1, drums	• No layers of confinement, filtered inner lid • No inner bags, no liner bags (bounding case)
Packaging Configuration 2, drums	• 1 inner bag • 1 filtered inner bag • 1 liner bag • 1 filtered liner bag • 1 inner bag, 1 liner bag • 1 filtered inner bag, 1 filtered liner bag • 2 inner bags • 2 filtered inner bags • 2 inner bags, 1 liner bag • 2 filtered inner bags, 1 filtered liner bag • 3 inner bags • 3 filtered inner bags • 3 filtered inner bags, 1 filtered liner bag • 3 inner bags, 1 liner bag (bounding case)
Packaging Configuration 3, drums	• 2 liner bags • 2 filtered liner bags • 1 inner bag, 2 liner bags • 1 filtered inner bag, 2 filtered liner bags • 2 inner bags, 2 liner bags • 2 filtered inner bags, 2 filtered liner bags • 3 filtered inner bags, 2 filtered liner bags • 4 inner bags • 3 inner bags, 2 liner bags • 4 inner bags, 2 liner bags (bounding case)
Packaging Configuration 4, pipe components	• No layers of confinement inside a pipe component • 1 filtered inner bag, 1 filtered metal can inside a pipe component • 2 inner bags inside a pipe component • 2 filtered inner bags inside a pipe component • 2 filtered inner bags, 1 filtered metal can inside a pipe component • 2 inner bags, 1 filtered metal can inside a pipe component (bounding case)
Packaging Configuration 5, Standard Waste Box	• No layers of confinement • 1 SWB liner bag (bounding case)
Packaging Configuration 6, Standard Waste Box	• any combination of inner and/or liner bags that is less than or equal to 6 • 5 inner bags, 1 SWB liner bag (bounding case)

a. 11. Attachment B1, Table B1-9

TABLE B1-9
SCENARIO 3 DRUM AGE CRITERIA (in days) MATRIX FOR S5000 WASTE
BY PACKAGING CONFIGURATION GROUP

Packaging Configuration 1						
	Liner Lid Hole Size					
Filter H_2 Diffusivity (mol/s/mol fraction)	0.3-inch Diameter Hole	0.375-inch Diameter Hole	0.75-inch Diameter Hole	1-inch Diameter Hole	No Liner Lid	No Liner
1.9×10^{-6}	131	95	37	24	4	4
3.7×10^{-6}	111	85	36	24	4	4
3.7×10^{-5}	28	28	23	19	4	4

Packaging Configuration 2						
	Liner Lid Hole Size					
Filter H_2 Diffusivity (mol/s/mol fraction)	0.3-inch Diameter Hole	0.375-inch Diameter Hole	0.75-inch Diameter Hole	1-inch Diameter Hole	No Liner Lid	No Liner
1.9×10^{-6}	175	138	75	60	30	11
3.7×10^{-6}	152	126	73	59	30	11
3.7×10^{-5}	58	57	52	47	28	8

Packaging Configuration 3						
	Liner Lid Hole Size					
Filter H_2 Diffusivity (mol/s/mol fraction)	0.3-inch Diameter Hole	0.375-inch Diameter Hole	0.75-inch Diameter Hole	1-inch Diameter Hole	No Liner Lid	No Liner
1.9×10^{-6}	197	161	96	80	46	16
3.7×10^{-6}	175	148[a]	93	79	46	16
3.7×10^{-5}	72	72	67	62	42	10

Packaging Configuration 4	
Filter H_2 Diffusivity (mol/s/mol fraction)	Headspace Sample Taken Inside Pipe Component
$> 1.9 \times 10^{-6}$	152

Packaging Configuration 5	
Filter H_2 Diffusivity [b] (mol/s/mol fraction)	**Headspace Sample Taken Inside SWB**
> 7.4 x 10^{-6}	15

Packaging Configuration 6	
Filter H_2 Diffusivity [b] (mol/s/mol fraction)	**Headspace Sample Taken Inside SWB**
> 7.4 x 10^{-6}	56

[a] A DAC of 142 days can be used for this case provided the packaging configuration does not exceed a total of 5 layers of confinement.

[b] The filter H_2 diffusivity for SWBs is the sum of the diffusivities for all of the filters on the SWB because an SWB has more than 1 filter.

a. 12. Attachment B1, Table B1-10

TABLE B1-10
SCENARIO 3 DRUM AGE CRITERIA (in days) MATRIX FOR S3000 AND S4000 WASTE BY PACKAGING CONFIGURATION GROUP

Packaging Configuration 1						
Filter H_2 Diffusivity (mol/s/mol fraction)	**0.3-inch Diameter Hole**	**0.375-inch Diameter Hole**	**0.75-inch Diameter Hole**	**1-inch Diameter Hole**	**No Lid**	**No Liner**
1.9×10^{-6}	131	95	37	24	4	4
3.7×10^{-6}	111	85	36	24	4	4
3.7×10^{-5}	28	28	23	19	4	4

Packaging Configuration 2						
Filter H_2 Diffusivity (mol/s/mol fraction)	**0.3-inch Diameter Hole**	**0.375-inch Diameter Hole**	**0.75-inch Diameter Hole**	**1-inch Diameter Hole**	**No Lid**	**No Liner**
1.9×10^{-6}	213	175	108	92	56	18
3.7×10^{-6}	188	161	105	90	56	17
3.7×10^{-5}	80	80	75	71	49	10

Packaging Configuration 3						
Filter H_2 Diffusivity (mol/s/mol fraction)	**0.3-inch Diameter Hole**	**0.375-inch Diameter Hole**	**0.75-inch Diameter Hole**	**1-inch Diameter Hole**	**No Lid**	**No Liner**
1.9×10^{-6}	283	243	171	154	107	34
3.7×10^{-6}	253	225	166	151	106	31
3.7×10^{-5}	121	121	115	110	84	13

Packaging Configuration 4	
Filter H_2 Diffusivity (mol/s/mol fraction)	**Headspace Sample Taken Inside Pipe Component**
$> 1.9 \times 10^{-6}$	152

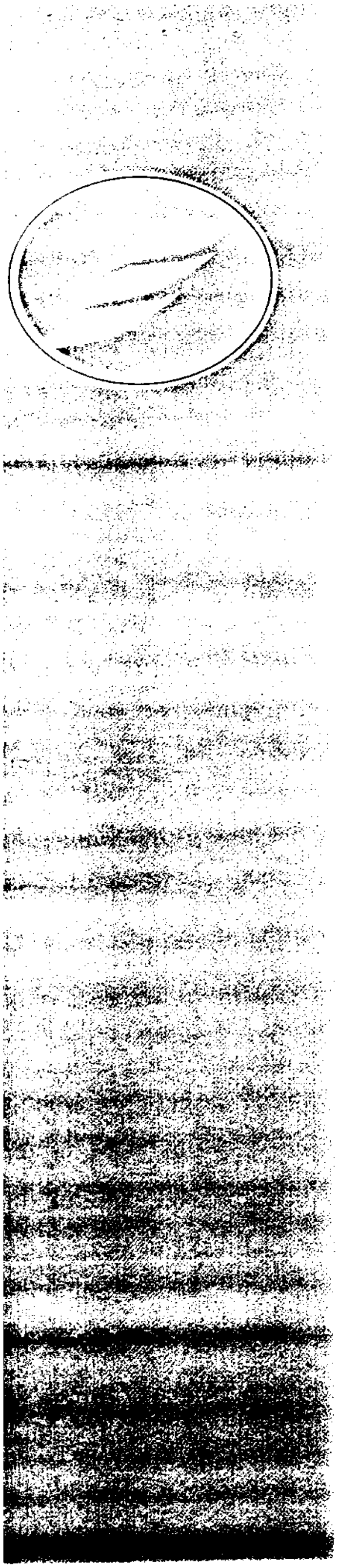
Packaging Configuration 5	
Filter H_2 Diffusivity [a] (mol/s/mol fraction)	**Headspace Sample Taken Inside SWB**
> 7.4 x 10^{-6}	15

Packaging Configuration 6	
Filter H_2 Diffusivity [a] (mol/s/mol fraction)	**Headspace Sample Taken Inside SWB**
> 7.4 x 10^{-6}	56

[a] The filter H_2 diffusivity for SWBs is the sum of the diffusivities for all of the filters on the SWB because an SWB has more than 1 filter.

Attachment B

Determination of Drum Age Criteria and Prediction Factors Based on Packaging Configurations INEEL/EXT-2000-01207



Idaho National Engineering and Environmental Laboratory

INEEL/EXT-2000-01207

October 2000

Determination of Drum Age Criteria and Prediction Factors Based on Packaging Configurations

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INEEL/EXT-2000-01207

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SUMMARY

The drum age criterion (DAC) is the time required to pass after drum closure, or after drum closure and drum venting, before a headspace gas sample can be collected. In an earlier report, drum age criteria were defined for two waste drum configurations under three different drum venting and sampling scenarios. The highest DAC values reported for each waste drum configuration are currently being used to define the minimum period of time required after drum venting before headspace gas sampling can occur. The application of only two specific DAC values to all waste drums require that sufficiently conservative assumptions were made regarding the waste drum configurations to ensure that the DACs represent the worst cases. Since the selection of the two DACs, other more restrictive waste packaging configurations have also been identified. As a result, there is currently no appropriate minimum waiting period identified for these waste drums. Furthermore, the availability of additional DACs for packaging configurations and sampling scenarios that better represent actual waste drums would result in shorter holding times between drum closure and drum gas sampling. In this report, additional DAC values are calculated for different venting and sampling scenarios as well as for a wider variety of waste drum packaging configurations. Model parameters and assumptions used in determining the DACs are documented.

Drum venting and sampling scenarios are defined by the time elapsed after drum closure and drum venting. Drum age criteria are defined for three unique drum venting and sampling scenarios:

Scenario 1: The drum liner headspace can be sampled at the time of venting if the waste drum was unvented for a period of time exceeding DAC_1.

The drum age criterion DAC_1 is defined as the time for a representative VOC to reach a concentration of at least 90% of it equilibrium concentration before drum venting. The drum age criterion DAC_1 for bounding waste packaging configuration used for Waste Types I and IV or S3000 (Homogeneous Solids) and S4000 (Soil/Gravel) was determined to be 127 days and for that used for Waste Types II and III or S5000 (Debris) waste was 53 days.

Scenario 2: If a waste drum is not vented until the DAC_1 has been exceeded, the drum headspace can be sampled in a vented drum after DAC_2 has been exceeded.

The drum age criterion DAC_2 is defined as the time for a representative VOC to reach a concentration of at least 90% of its steady-state concentration after venting a waste drum that was unvented for at least DAC_1. DAC_2 values are calculated for the two waste configurations under Scenario 1 with four different opening sizes in the punctured drum liner lid and three different drum filter vents. DAC_2 values range from 4 to 36 days. In this scenario, a single DAC is not to be defined by adding DAC_1 and DAC_2 values. DAC_1 and DAC_2 are separate drum age criteria, which must both be met.

Scenario 3: If DAC_1 is not met when the drum is vented, the drum headspace can be sampled after the DAC_3 has been exceeded. For newly generated drums that were vented at the time of generation, the drum headspace can also be sampled after the DAC_3 has been exceeded.

The drum age criterion DAC_3 is defined as the time for a representative VOC to reach a concentration within at least 10% of its steady-state concentration. DAC_3 values are calculated for the two category waste types and for each of the three different packaging configurations representing

different layers of polymer bags with five different opening sizes in the drum liner lid as well as the case of no rigid liner inside the drum and three different drum filter vents. Nearly 100 DAC_3 values are calculated and range between 4 and 283 days. A considerable number of the DAC_3 values are less than the current DAC values of 142 and 225 days. DAC_3 values were also calculated for packaging configurations that included standard waste boxes (SWBs) and pipe components (sampling inside the pipe component headspace). The DAC_3 values calculated for the SWBs and the pipe component were intended to conservatively bound the wide range of likely packaging configurations. The methodology used to determine prediction factors that relate the measured VOC concentration in the container headspace to the VOC concentration in the innermost confinement layer is also presented.

The concept of a DAC can be impractical for waste containers with a highly restrictive packaging configuration, which may require an extremely long time to achieve steady state. This can be expected of waste drums containing metal cans and pipe overpacks. "Pipe Overpack" is a vented 55-gallon drum containing a pipe component. For pipe overpacks and drums containing metal cans, a more time-efficient methodology is outlined to evaluate the VOC concentration in the drum headspace after a given period of time and relating it to the steady-state VOC headspace concentration. A VOC concentration multiplier is defined as the ratio of 90% of the steady-state VOC concentration in the sampling headspace divided by the VOC headspace concentration at a given time. The use of these multipliers and steady-state prediction factors can be used to relate the measured VOC concentration in the drum headspace to the steady-state VOC concentration within the innermost layer of confinement. The VOC concentration multipliers were calculated using the same equations that are used to calculate DACs. Multipliers for three bounding packaging configurations involving pipe overpack and metal cans with two possible filter vents as well as two different filter vents for the waste drum were calculated as a function of drum age. Lower multipliers for older drums take credit for the higher drum headspace concentration that can be expected with increasing drum age.

The calculation of DACs for three common drum venting and sampling scenarios provides more realistic waiting periods for sampling than current DACs. For example, DAC_2 values indicate that unvented drums that have been in storage in excess of DAC_1 values (53 or 127 days) can be realistically sampled in anywhere from 4 to 36 days depending on the liner lid opening and drum filter vent installed at the time of venting. This could provide relief (compared to current DACs of 142 or 225 days) of over 200 days in some cases in reducing the waiting time required before sampling the drum headspace. The DAC values calculated for the SWBs and the pipe component were intended to conservatively bound the wide range of likely packaging configurations. In the case of the pipe component, the DAC is the waiting time required before sampling directly from the pipe component headspace. This DAC does not apply to pipe overpacks for which VOC concentration multipliers can be used.

CONTENTS

Determination of Drum Age Criteria and Prediction Factors Based on Packaging Configurations

1. BACKGROUND

Transuranic (TRU) waste drums must meet a minimum age criterion before a gas sample collected from the waste drum is considered representative of the total drum headspace. The drum age criterion (DAC) is the time required to pass after drum closure, or after drum closure and drum venting, before a headspace gas sample can be collected. The manner in which the DACs are defined is dependent on when drum venting and headspace gas sampling occur (Connolly et al., 1998). Drum age criteria were defined for two waste drum configurations under three different drum venting and sampling scenarios. The waste drum configurations were selected to represent the worst cases of common packaging configurations. In each combination of waste drum configuration and sampling scenario, the DAC was defined as the time necessary for the concentration of a representative volatile organic compound (VOC) in the sampling headspace to be within at least 10% of its final steady-state or equilibrium concentration (Connolly et al., 1998). From these three sampling scenarios, the highest DAC values reported for each waste drum configuration were used to define the minimum period of time required before headspace gas sampling can occur.

The DAC values are a strong function of the waste packaging configuration. Packaging parameters include the number of layers of polymer bags surrounding the waste, the thickness and surface area of the polymer bags, the presence or absence of a rigid polymer drum liner and it's characteristics, and the gas diffusion characteristic of the drum filter vent. The application of only two specific DAC values to all waste drums require that sufficiently conservative assumptions were made regarding the waste drum configurations to ensure that the DACs represent the worst cases. Since the generation of the two DACs, other more restrictive waste packaging configurations have been identified. As a result, there is currently no appropriate minimum waiting period identified for these waste drums. Furthermore, the availability of additional DACs for packaging configurations and sampling scenarios that better represent actual waste drums would result in shorter holding times between drum closure and drum gas sampling.

2. PURPOSE AND SCOPE

Additional DAC values are calculated for different venting and sampling scenarios as well as for a wider variety of waste drum packaging configurations. Model parameters and assumptions used in determining the DACs are documented. The concept of a VOC concentration multiplier is described and a time-efficient methodology is outlined, which relates the measured VOC drum headspace concentration of waste containers with a highly restrictive packaging configuration to its steady-state VOC headspace concentration. Equations defining prediction factors relating the measured VOC concentration to the VOC concentration within the innermost layer of confinement are detailed.

3. PREVIOUS DAC CALCULATIONS

The current limits for DACs (Connolly et al., 1998) are categorized based on the waste form and packaging as follows:

Waste Types I and IV, Solidified Inorganics and Solidified Organics. These wastes were assumed to be packaged in two drum liner bags, in a rigid drum liner with a 0.375-inch diameter hole, in a 55-gallon drum fitted with a filter with a hydrogen diffusivity of 4.2E-06 moles/second/mole fraction.

Waste Types II and III, Solid Inorganics and Solid Organics. These wastes were assumed to be packaged in three inner bags and two drum liner bags, in a rigid drum liner with a 0.375-inch diameter hole, in a 55-gallon drum fitted with a filter with a hydrogen diffusivity of 4.2E-06 moles/second/mole fraction.

The drum age criteria were determined for these waste packaging configurations and the following venting and sampling scenarios (Connolly et al., 1998):

1. **Containers that are unvented and are sampled under the rigid liners at the time of venting.**

The drum age criterion is the time required for a representative VOC to achieve a concentration of at least 90% of its equilibrium concentration in the drum liner headspace before venting. A representative VOC is a compound that is significant and yields the highest DAC (Connolly et al., 1998). For drums containing Waste Types I/IV drums, a DAC of 127 days was calculated. For drums containing Waste Types II/III, a DAC of 48 days was calculated.

2. **Containers that have been packaged for a specified period of time sufficient to achieve equilibrium conditions and then are vented.**

In this case, the total waiting time before headspace sampling is the time after drum closure to achieve equilibrium conditions and the time between venting and sampling for the drum headspace concentration of a representative VOC to be within at least 10% of its steady-state concentration. In the case where complete equilibrium had been achieved before drum venting, the DACs after venting were calculated to be 22 and 18 days for Waste Types I/IV and Waste Types II/III, respectively.

3. **Containers that are initially packaged in a vented condition.**

The drum age criterion is defined as the time for a representative VOC to reach a concentration that is at least 90% of its steady-state concentration in the drum headspace. For drums containing Waste Types I/IV drums, a DAC of 225 days was calculated. For drums containing Waste Types II/III, a DAC of 142 days was calculated. These DACs were the highest values calculated for the three venting and sampling scenarios.

The DAC for each case was determined using a computer program that solved a series of differential equations describing the VOC transport phenomena within the waste drum. Model input parameters include the physical properties of the VOC, the initial concentration profile in the drum, physical dimensions of each layer of confinement (thickness, surface area, void volume), and the hydrogen diffusion characteristic of the drum filter vent. Other model input parameters and model assumptions are described in Connolly et al. (1998).

4. DEFINING BOUNDING DRUM AGE CRITERIA

The past work (Connolly et al., 1998) determining DACs for specific waste packaging configurations as well as a sensitivity analysis to identify the most important parameters that influence the calculated DAC (Liekhus et al. 1999) serves as the foundation for calculating DACs for different venting and sampling scenarios as well as for a wider variety of waste drum packaging configurations. The sensitivity analysis indicated that filter vent characteristic, opening size in liner lid, as well as the presence or absence of the liner itself had a significant influence on the DAC values. Variables such as total bag thickness and the presence or absence of bag filters had little influence.

Drum age criteria are defined for three unique drum venting and sampling scenarios. These drum venting and sampling scenarios are defined by the time elapsed after drum closure and drum venting:

t_1 – time (days) elapsed after drum closure until drum venting

t_2 – time (days) elapsed after drum venting

Scenario 1: The drum liner headspace can be sampled at the time of venting if t_1 is greater than DAC_1.

The drum age criterion DAC_1 is defined as the time for a representative VOC to reach a concentration of at least 90% of its equilibrium concentration before drum venting. Two waste drum configurations are considered:

1. Drum liner with two polymer drum liners bags

This packaging configuration is assumed for S3000 (Homogeneous solids) and S4000 (Soil/gravel) wastes. This corresponds to Waste Types I and IV (Connolly et al., 1998).

2. Drum liner with four polymer inner bags and two polymer drum liners bags

This packaging configuration is assumed for S5000 (Debris) waste. This configuration is similar to that assumed for Waste Types II and III (Connolly et al., 1998) except that the assumption of six polymer bags is considered to represent the bounding case.

The DAC_1 values for these two configurations are listed in Table 1. The model input parameters used to calculate these results are listed in Appendix A.

Table 1. DAC_1 values for S3000/S4000 (Waste Types I and IV) and S5000 (Waste Types II and III) waste.

Waste Type	DAC_1 (days)
S3000/S4000 (Waste Types I and IV)	127
S5000 (Waste Types II and III)	53

Scenario 2: The drum headspace can be sampled in a vented drum if t_1 is greater than DAC_1, and t_2 is greater than DAC_2.

The drum age criterion DAC_2 is defined as the time for a representative VOC to reach a headspace concentration within at least 10% of its steady-state concentration after venting a waste drum that was unvented for at least DAC_1. DAC_2 values are calculated for the two waste configurations under Scenario 1 with four different opening sizes in the punctured drum liner lid and three different drum filter vents. The DAC_2 values are listed in Table 2. The model input parameters used to calculate these results are listed in Appendix A.

A single DAC is not defined by adding DAC_1 and DAC_2. DAC_1 and DAC_2 are separate drum age criteria which must both be met under this scenario. If not, scenario 3 should be used.

Table 2. DAC_2 values for S3000/S4000 (Waste Types I and IV) and S5000 (Waste Types II and III) waste.

	S3000/S4000 (Waste Types I and IV)				S5000 (Waste Types II and III)			
Drum Filter Vent	Liner Lid Opening Diameter (in)				Liner Lid Opening Diameter (in)			
D^*_{H2} (mol/s/mol fr)	0.30	0.375	0.75	1.0	0.30	0.375	0.75	1.0
1.9×10^{-6}	36	30	23	22	29	22	13	12
3.7×10^{-6}	30	25	19	18	25	20	12	11
3.7×10^{-5}	13	11	11	11	7	6	6	4

Scenario 3: If t_1 is less than DAC_1 when the drum is vented, the drum headspace can be sampled when t_2 is greater than DAC_3. Also for newly generated drums that were vented at the time of generation, the drum headspace can be sampled after the DAC_3 has been exceeded.

The drum age criterion DAC_3 is defined as the time for a representative VOC to reach a headspace concentration of at least 90% of its steady-state concentration. DAC_3 values are calculated for the two categories of waste types each with three different packaging configurations representing different layers of polymer bags with five different opening sizes in the drum liner lid as well as the case of no rigid liner inside the drum and three different drum filter vents. The model input parameters used to calculate these results are listed in Appendix A. The DAC_3 values are listed in Tables 3 and 4.

Table 3. DAC_3 values for S3000/S4000 (Waste Types I and IV) waste packaging configurations.

		Liner Lid Opening					
Packaging Configuration	Filter Vent H_2 Diffusion Characteristic (mol/s/mol fr.)	0.30-in diameter	0.375-in diameter	0.75-in diameter	1-in diameter	No Lid	No Liner
No bags	1.9×10^{-6}	131	95	37	24	4	4 [a]
No bags	3.7×10^{-6}	111	85	36	24	4	4 [a]
No bags	3.7×10^{-5}	28	28	23	19	4	4 [a]
One liner bag	1.9×10^{-6}	213	175	108	92	56	18
One liner bag	3.7×10^{-6}	188	161	105	90	56	17
One liner bag	3.7×10^{-5}	80	80	75	71	49	10
Two liner bags	1.9×10^{-6}	283	243	171	154	107	34
Two liner bags	3.7×10^{-6}	253	225	166	151	106	31
Two liner bags	3.7×10^{-5}	121	121	115	110	84	13

[a] - DACs not calculated and assumed to be same as case of liner with no lid.

Table 4. DAC_3 values for S5000 (Waste Types II and III) waste packaging configurations.

		Liner Lid Opening					
Packaging Configuration	Filter Vent H_2 Diffusion Characteristic (mol/s/mol fr.)	0.30-in diameter	0.375-in diameter	0.75-in diameter	1-in diameter	No Lid	No Liner
No bags	1.9×10^{-6}	131	95	37	24	4	4[a]
No bags	3.7×10^{-6}	111	85	36	24	4	4[a]
No bags	3.7×10^{-5}	28	28	23	19	4	4[a]
3 IBs, 1 LB	1.9×10^{-6}	175	138	75	60	30	11
3 IBs, 1 LB	3.7×10^{-6}	152	126[b]	73	59	30	11
3 IBs, 1 LB	3.7×10^{-5}	58	57	52	47	28	8
4 IBs, 2 LBs	1.9×10^{-6}	197	161	96	80	46	16
4 IBs, 2 LBs	3.7×10^{-6}	175	148[b]	93	79	46	16
4 IBs, 2 LBs	3.7×10^{-5}	72	72	67	62	42	10

IB=inner bag, LB=liner bag,

[a] DACs not calculated and assumed to be same as case of liner with no lid.

[b] DAC=142 days (Connolly et al., 1998) based on packaging configuration on 3 IBs, 2LBs, filter vent=4.2×10^{-6} mol/s/mol fr.

DAC_3 values were also calculated for packaging configurations other than waste drums. These configurations included standard waste boxes (SWBs) and pipe components. Two SWB configurations and one pipe component configuration intended to serve as a bounding case were considered. The SWB packing configuration 1 assumes waste wrapped inside 5 inner bags is placed in a single liner bag in a SWB. The SWB packaging configuration 2 assumes waste is directly placed inside a single liner bag in a SWB. The SWB has two or more filter vents with a total hydrogen diffusion characteristic of 7.4×10^{-6} mol/s/mol fr. The packaging configuration of 2 polymer bags surrounding waste in a vented metal can inside a vented pipe component is intended to represent the bounding case for waste packaged inside a pipe component. The sampling in this case is required inside the headspace of the pipe component itself. In the case of the pipe component the model input parameters used to calculate these DAC_3 values are listed in Appendix A. The DACs for these packaging configurations are listed in Table 5.

Table 5. DAC_3 values for special packaging configuration.

Waste Packaging Configuration	DAC (days)[a]
SWB (5 layers inner bags, one SWB liner bag)	56
SWB (one SWB liner bag)	15
Pipe component (2 inner bags, vented metal can)	152

[a] Applies to sampling directly from SWB or pipe component.

5. VOC CONCENTRATION MULTIPLIERS

The concept of a DAC (time to achieve 90% of steady-state concentration) for sampling vented waste drum headspace can be impractical for waste containers with a highly restrictive packaging configuration which may require an extremely long time to achieve steady state. This can be expected of waste drum containing metal cans and pipe overpacks. "Pipe Overpack" is a vented 55-gallon drum containing a pipe component. For these cases, a more time-efficient methodology is outlined to evaluate the VOC concentration in the drum headspace after a given period of time and relating it to the steady-state VOC headspace concentration.

A VOC concentration multiplier is defined as the ratio of 90% of the steady-state VOC concentration in the sampling headspace divided by the VOC headspace concentration at a given time. This ratio can be calculated using the same differential equations as are in the computer program (VDRUM.FOR) that determines the DACs. The software program was revised to allow for a greater number of layers of confinement, multiple mechanisms for VOC transport to occur simultaneously across each layer of confinement, and greater flexibility in program output. The revised computer code, VDRUM2.FOR, was created, verified, and validated (Liekhus and Chambers, 2000). The VOC concentration multipliers were calculated as a function of the waste drum age for three bounding packaging configurations involving vented pipe components and metal cans with two possible filter vents as well as two different filter vents for the waste drum using the code VDRUM2.FOR. Lower multipliers for older drums take credit for the higher drum headspace concentration that can be expected with increasing drum age. The VOC concentration multipliers associated with vented drum headspace sampling of drums containing vented pipe components or vented metal cans are tabulated in Tables 6 through 9. The model input parameters used to calculate the VOC concentration multipliers are listed in Appendix B.

Table 6. VOC Concentration Multipliers ($D^*_{H2,drum} = D^*_{H2,can} = 1.9e\text{-}6$ mol/s/mol fr.) as a function of time (days) after venting.

		Waste Drum Packaging Configuration											
		2IB-PC-DL-DF*				3IB-FC-2LB-DL-DF*				2IB-FC-PC-DL-DF*			
Volatile Organic Compound	Days	75	150	300	600	75	150	300	600	75	150	300	600
carbon tetrachloride		5.5	2.9	1.7	1.1	7.8	3.9	2.2	1.4	14.9	5.4	2.4	1.4
cyclohexane		6.6	2.6	1.4	1.0	11.6	4.2	1.9	1.2	10.5	3.8	1.8	1.1
methanol		2.8	1.8	1.2	1.0	4.0	2.4	1.5	1.1	5.3	2.6	1.5	1.1
dichloromethane		3.2	1.8	1.2	1.0	4.5	2.5	1.5	1.1	7.5	3.1	1.6	1.1
toluene		22.7	11.5	6.0	3.2	32.6	15.5	7.7	4.0	64.9	22.9	9.5	4.5
trichloroethane		4.3	2.3	1.4	1.0	6.2	3.2	1.8	1.2	11.2	4.2	2.0	1.2
trichloroethylene		11.2	5.7	3.1	1.8	15.4	7.6	4.0	2.2	31.2	11.1	4.8	2.4
Freon-13		4.5	2.1	1.3	1.0	6.7	3.1	1.7	1.1	9.9	3.6	1.7	1.1
p-xylene		45.1	22.8	11.7	6.1	74.4	33.2	15.7	7.8	136.9	47.6	19.2	8.8
acetone		3.1	1.8	1.2	1.0	4.5	2.4	1.5	1.1	7.4	2.9	1.5	1.0
butanol		4.8	2.6	1.6	1.1	6.7	3.5	2.0	1.3	12.7	4.8	2.2	1.3
chloroform		3.5	2.0	1.3	1.0	5.0	2.7	1.6	1.1	8.9	3.5	1.7	1.1
1,1-dichloroethene		3.3	1.8	1.2	1.0	4.8	2.5	1.5	1.1	7.8	3.0	1.5	1.0
methyl ethyl ketone		4.1	2.2	1.4	1.0	5.8	3.0	1.8	1.2	10.3	3.9	1.9	1.2
methyl isobutyl ketone		7.1	3.6	2.0	1.3	10.1	5.0	2.7	1.6	19.6	6.9	3.0	1.6
1,1,2,2-tetrachloroethane		17.0	8.8	4.6	2.6	23.8	11.6	5.9	3.1	49.4	17.5	7.3	3.6
tetrachloroethene		9.1	4.7	2.6	1.6	12.5	6.3	3.3	1.9	26.4	9.4	4.0	2.1
benzene		4.2	2.3	1.4	1.0	5.9	3.1	1.8	1.2	10.7	4.1	2.0	1.2
bromoform		20.1	10.3	5.4	3.0	28.5	13.7	6.9	3.6	57.2	20.4	8.6	4.1
chlorobenzene		10.2	5.3	2.9	1.7	14.1	7.0	3.7	2.1	29.7	10.6	4.5	2.3
1,1-dichloroethane		3.3	1.9	1.2	1.0	4.8	2.6	1.5	1.1	8.3	3.3	1.6	1.1
1,2-dichloroethane		4.5	2.5	1.5	1.1	6.2	3.3	1.9	1.2	11.7	4.5	2.1	1.3
cis-1,2-dichloroethene		3.4	1.9	1.2	1.0	4.8	2.6	1.5	1.1	8.4	3.3	1.7	1.1
ethylbenzene		10.8	5.4	2.9	1.7	15.1	7.4	3.9	2.2	31.5	11.0	4.6	2.3
ethyl ether		4.1	2.0	1.2	1.0	6.1	2.9	1.6	1.1	8.4	3.2	1.6	1.1
1,3,5-trimethylbenzene		18.1	9.0	4.7	2.6	26.1	12.4	6.2	3.3	55.9	19.0	7.6	3.6
1,2,4-trimethylbenzene		20.6	10.3	5.3	2.9	30.0	14.1	7.0	3.7	64.3	21.8	8.7	4.1
o-xylene		12.4	6.3	3.4	1.9	17.4	8.5	4.4	2.4	36.9	12.9	5.3	2.6
m-xylene		10.8	5.5	2.9	1.7	15.2	7.4	3.9	2.2	31.8	11.1	4.6	2.3

*IB-Inner bag; PC-vented pipe component; FC-filtered can; LB-drum liner bag; DL-drum liner; DF-drum filter vent

Table 7. VOC Concentration Multipliers ($D^*_{H2,drum}$ = 1.9e-6 mol/s/mol fr.; $D^*_{H2,can}$ = 3.7e-6 mol/s/mol fr.) as a function of time (days) after venting.

		Waste Drum Packaging Configuration											
		2IB-PC-DL-DF*				3IB-FC-2LB-DL-DF*				2IB-FC-PC-DL-DF*			
Volatile Organic Compound	Days	75	150	300	600	75	150	300	600	75	150	300	600
carbon tetrachloride		4.1	2.2	1.4	1.0	6.2	3.2	1.8	1.2	8.5	3.6	1.9	1.2
cyclohexane		5.0	2.2	1.3	1.0	11.1	4.1	1.9	1.2	7.1	2.9	1.6	1.1
methanol		2.3	1.5	1.1	1.0	3.5	2.2	1.4	1.0	3.6	2.1	1.3	1.0
dichloromethane		2.4	1.5	1.1	1.0	3.6	2.0	1.3	1.0	4.6	2.2	1.3	1.0
toluene		15.8	8.1	4.3	2.4	23.5	11.2	5.7	3.0	35.3	14.4	6.7	3.4
trichloroethane		3.2	1.8	1.2	1.0	5.1	2.7	1.6	1.1	6.6	2.9	1.6	1.1
trichloroethylene		7.9	4.1	2.3	1.4	11.2	5.6	3.0	1.7	17.2	7.1	3.5	1.9
Freon-13		3.5	1.8	1.1	1.0	6.1	2.9	1.6	1.1	6.3	2.7	1.5	1.0
p-xylene		31.1	15.8	8.2	4.3	52.7	23.5	11.2	5.7	72.8	29.2	13.3	6.5
acetone		2.4	1.4	1.0	1.0	3.8	2.1	1.3	1.0	4.6	2.1	1.3	1.0
butanol		3.5	2.0	1.3	1.0	5.2	2.8	1.6	1.1	7.3	3.2	1.7	1.1
chloroform		2.6	1.6	1.1	1.0	3.9	2.2	1.4	1.0	5.3	2.4	1.4	1.0
1,1-dichloroethene		2.5	1.5	1.0	1.0	4.1	2.2	1.4	1.0	4.8	2.2	1.3	1.0
methyl ethyl ketone		3.1	1.7	1.2	1.0	4.8	2.5	1.5	1.1	6.1	2.7	1.5	1.1
methyl isobutyl ketone		5.3	2.7	1.6	1.1	8.3	4.1	2.3	1.4	11.2	4.6	2.3	1.4
1,1,2,2-tetrachloroethane		11.8	6.1	3.3	1.9	16.5	8.1	4.2	2.3	26.6	11.0	5.2	2.7
tetrachloroethene		6.4	3.4	2.0	1.3	9.1	4.6	2.5	1.5	14.4	6.0	2.9	1.7
benzene		3.1	1.8	1.2	1.0	4.6	2.5	1.5	1.1	6.3	2.8	1.6	1.1
bromoform		13.8	7.2	3.8	2.2	19.6	9.5	4.9	2.6	30.9	12.8	6.0	3.1
chlorobenzene		7.2	3.8	2.2	1.4	10.3	5.2	2.8	1.7	16.2	6.7	3.3	1.8
1,1-dichloroethane		2.5	1.5	1.1	1.0	3.9	2.1	1.3	1.0	5.0	2.3	1.3	1.0
1,2-dichloroethane		3.3	1.9	1.2	1.0	4.7	2.5	1.5	1.1	6.7	3.0	1.7	1.1
cis-1,2-dichloroethene		2.5	1.5	1.1	1.0	3.8	2.1	1.3	1.0	5.0	2.3	1.4	1.0
ethylbenzene		7.7	4.0	2.2	1.4	11.5	5.7	3.0	1.8	17.3	7.0	3.3	1.9
ethyl ether		3.3	1.7	1.1	1.0	5.6	2.7	1.5	1.1	5.5	2.4	1.4	1.0
1,3,5-trimethylbenzene		12.8	6.5	3.4	2.0	19.7	9.4	4.8	2.6	30.1	11.8	5.4	2.8
1,2,4-trimethylbenzene		14.5	7.3	3.9	2.2	22.3	10.6	5.3	2.9	34.3	13.4	6.1	3.1
o-xylene		8.8	4.6	2.5	1.5	13.0	6.4	3.4	1.9	20.0	8.1	3.8	2.1
m-xylene		7.7	4.0	2.2	1.4	11.6	5.7	3.0	1.8	17.4	7.0	3.4	1.9

*IB-Inner bag; PC-vented pipe component; FC-filtered can; LB-drum liner bag; DL-drum liner; DF-drum filter vent

Table 8. VOC Concentration Multipliers ($D^*_{H2,drum}$ = 3.7e-6 mol/s/mol fr.; $D^*_{H2,can}$ = 1.9e-6 mol/s/mol fr.) as a function of time (days) after venting.

		Waste Drum Packaging Configuration											
		2IB-PC-DL-DF*				3IB-FC-2LB-DL-DF*				2IB-FC-PC-DL-DF*			
Volatile Organic Compound	Days	75	150	300	600	75	150	300	600	75	150	300	600
carbon tetrachloride		3.9	2.1	1.3	1.0	5.3	2.8	1.6	1.1	9.3	3.5	1.7	1.1
cyclohexane		4.3	1.9	1.1	1.0	6.9	2.6	1.4	1.0	6.4	2.5	1.3	1.0
methanol		2.1	1.4	1.1	1.0	2.8	1.8	1.2	1.0	3.5	1.9	1.2	1.0
dichloromethane		2.3	1.4	1.0	1.0	3.2	1.8	1.2	1.0	4.8	2.1	1.2	1.0
toluene		15.5	7.9	4.2	2.3	22.3	10.7	5.4	2.9	40.0	14.2	6.0	3.0
trichloroethane		3.0	1.7	1.1	1.0	4.2	2.3	1.4	1.0	7.1	2.8	1.4	1.0
trichloroethylene		7.7	4.0	2.3	1.4	10.6	5.3	2.8	1.7	19.4	7.0	3.1	1.7
Freon-13		3.2	1.6	1.1	1.0	4.3	2.1	1.3	1.0	6.2	2.4	1.3	1.0
p-xylene		30.7	15.6	8.0	4.3	50.7	22.7	10.9	5.5	84.1	29.4	11.9	5.6
acetone		2.3	1.4	1.0	1.0	3.1	1.8	1.2	1.0	4.8	2.0	1.2	1.0
butanol		3.4	1.9	1.2	1.0	4.7	2.5	1.5	1.1	8.0	3.1	1.6	1.1
chloroform		2.5	1.5	1.1	1.0	3.5	2.0	1.3	1.0	5.7	2.4	1.3	1.0
1,1-dichloroethene		2.3	1.4	1.0	1.0	3.3	1.8	1.2	1.0	5.0	2.1	1.2	1.0
methyl ethyl ketone		2.9	1.6	1.1	1.0	4.0	2.2	1.4	1.0	6.5	2.6	1.4	1.0
methyl isobutyl ketone		4.9	2.6	1.5	1.1	6.8	3.4	1.9	1.2	12.2	4.4	2.0	1.2
1,1,2,2-tetrachloroethane		11.7	6.1	3.3	1.9	16.5	8.1	4.2	2.3	30.6	11.0	4.7	2.4
tetrachloroethene		6.3	3.4	1.9	1.3	8.6	4.4	2.4	1.5	16.4	6.0	2.7	1.5
benzene		3.0	1.7	1.2	1.0	4.1	2.2	1.4	1.0	6.8	2.7	1.4	1.0
bromoform		13.8	7.2	3.8	2.2	19.7	9.6	4.9	2.7	35.4	12.7	5.4	2.7
chlorobenzene		7.1	3.7	2.1	1.3	9.7	4.9	2.7	1.6	18.4	6.7	3.0	1.6
1,1-dichloroethane		2.4	1.4	1.0	1.0	3.3	1.9	1.2	1.0	5.4	2.2	1.2	1.0
1,2-dichloroethane		3.2	1.8	1.2	1.0	4.4	2.4	1.5	1.1	7.4	3.0	1.5	1.0
cis-1,2-dichloroethene		2.4	1.5	1.1	1.0	3.4	1.9	1.2	1.0	5.4	2.3	1.3	1.0
ethylbenzene		7.4	3.8	2.1	1.4	10.3	5.1	2.7	1.6	19.5	6.9	3.0	1.6
ethyl ether		2.9	1.5	1.0	1.0	3.9	2.0	1.2	1.0	5.3	2.2	1.2	1.0
1,3,5-trimethylbenzene		12.4	6.2	3.3	1.9	17.7	8.4	4.3	2.4	34.4	11.8	4.8	2.4
1,2,4-trimethylbenzene		14.1	7.1	3.7	2.1	20.3	9.7	4.9	2.7	39.6	13.6	5.5	2.7
o-xylene		8.5	4.4	2.4	1.5	11.9	5.9	3.1	1.8	22.8	8.1	3.5	1.8
m-xylene		7.4	3.8	2.2	1.4	10.3	5.1	2.8	1.6	19.7	7.0	3.0	1.6

*IB-Inner bag; PC-vented pipe component; FC-filtered can; LB-drum liner bag; DL-drum liner; DF-drum filter vent

Table 9. VOC Concentration Multipliers ($D^*_{H2,drum} = D^*_{H2,can}$ = 3.7e-6 mol/s/mol fr.) as a function of time (days) after venting.

		Waste Drum Packaging Configuration											
		2IB-PC-DL-DF*				3IB-FC-2LB-DL-DF*				2IB-FC-PC-DL-DF*			
Volatile Organic Compound	Days	75	150	300	600	75	150	300	600	75	150	300	600
carbon tetrachloride		3.1	1.8	1.2	1.0	4.5	2.4	1.5	1.1	5.8	2.6	1.4	1.0
cyclohexane		3.4	1.6	1.1	1.0	6.7	2.6	1.4	1.0	4.4	2.0	1.2	1.0
methanol		1.8	1.3	1.0	1.0	2.6	1.7	1.2	1.0	2.6	1.6	1.1	1.0
dichloromethane		1.9	1.3	1.0	1.0	2.7	1.6	1.1	1.0	3.2	1.7	1.1	1.0
toluene		12.0	6.2	3.3	1.9	17.6	8.5	4.4	2.4	23.9	9.8	4.7	2.5
trichloroethane		2.5	1.5	1.0	1.0	3.7	2.0	1.3	1.0	4.6	2.1	1.2	1.0
trichloroethylene		6.0	3.2	1.9	1.2	8.5	4.3	2.4	1.4	11.7	5.0	2.5	1.5
Freon-13		2.6	1.4	1.0	1.0	4.1	2.0	1.2	1.0	4.2	1.9	1.2	1.0
p-xylene		23.6	12.0	6.3	3.4	39.6	17.8	8.6	4.4	49.1	19.8	9.1	4.5
acetone		1.9	1.2	1.0	1.0	2.8	1.6	1.1	1.0	3.2	1.6	1.1	1.0
butanol		2.8	1.6	1.1	1.0	3.9	2.2	1.4	1.0	5.1	2.3	1.4	1.0
chloroform		2.1	1.3	1.0	1.0	3.0	1.7	1.2	1.0	3.7	1.8	1.1	1.0
1,1-dichloroethene		2.0	1.2	1.0	1.0	2.9	1.7	1.1	1.0	3.3	1.6	1.1	1.0
methyl ethyl ketone		2.4	1.4	1.0	1.0	3.5	1.9	1.3	1.0	4.2	2.0	1.2	1.0
methyl isobutyl ketone		4.0	2.1	1.3	1.0	5.9	3.0	1.7	1.2	7.6	3.2	1.7	1.1
1,1,2,2-tetrachloroethane		9.0	4.8	2.6	1.6	12.7	6.3	3.3	1.9	18.1	7.6	3.7	2.0
tetrachloroethene		4.9	2.7	1.6	1.1	6.9	3.6	2.0	1.3	9.9	4.2	2.1	1.3
benzene		2.4	1.5	1.1	1.0	3.5	1.9	1.3	1.0	4.4	2.1	1.2	1.0
bromoform		10.6	5.6	3.0	1.8	15.0	7.3	3.8	2.1	21.1	8.8	4.2	2.3
chlorobenzene		5.5	3.0	1.8	1.2	7.8	4.0	2.2	1.4	11.0	4.7	2.4	1.4
1,1-dichloroethane		2.0	1.3	1.0	1.0	2.9	1.7	1.1	1.0	3.5	1.7	1.1	1.0
1,2-dichloroethane		2.6	1.5	1.1	1.0	3.6	2.0	1.3	1.0	4.7	2.2	1.3	1.0
cis-1,2-dichloroethene		2.0	1.3	1.0	1.0	2.9	1.7	1.1	1.0	3.5	1.7	1.1	1.0
ethylbenzene		5.9	3.1	1.8	1.2	8.5	4.3	2.3	1.4	11.7	4.8	2.4	1.4
ethyl ether		2.4	1.3	1.0	1.0	3.7	1.9	1.2	1.0	3.7	1.7	1.1	1.0
1,3,5-trimethylbenzene		9.7	4.9	2.7	1.6	14.5	7.0	3.6	2.0	20.2	8.0	3.8	2.0
1,2,4-trimethylbenzene		11.0	5.6	3.0	1.8	16.5	7.9	4.0	2.2	23.1	9.2	4.3	2.3
o-xylene		6.7	3.5	2.0	1.3	9.7	4.8	2.6	1.6	13.6	5.6	2.7	1.6
m-xylene		5.9	3.1	1.8	1.2	8.5	4.3	2.4	1.4	11.8	4.9	2.4	1.4

*IB-Inner bag; PC-vented pipe component; FC-filtered can; LB-drum liner bag; DL-drum liner; DF-drum filter vent

6. PREDICTION FACTOR METHODOLOGY

The prediction factor (PF) is a variable with a unique value for each VOC and packaging configuration that, when multiplied by the measured VOC concentration in the container headspace, predicts the VOC concentration in the innermost confinement layer. Prediction factors are not required with Scenario 1; however, they are used in conjunction with Scenario 2 and 3 when inner layer of confinement VOC concentration ratios are required. This section describes the methodology used for the determination of PFs. This methodology is based on the analysis presented in Connolly et al. (1998).

At steady conditions, there is no accumulation of VOC within any layer of confinement, the concentrations of VOCs are constant within each layer of confinement and the VOC transport rate across each layer of confinement is equal to a constant rate. The primary mechanisms for gas transport across a confinement layer are permeation across a polymeric layer, diffusion through air across an opening in the layer, and diffusion through a filter vent in the case of a filtered bag. One or all these mechanisms of transport may be operating depending on the characteristics of the confinement layer.

6.1 Model Assumptions

The following assumptions are made in developing the PF methodology:

1. All gases exhibit ideal behavior.

2. Temperature and pressure are constant.

3. An equilibrium exists between the VOC-contaminated waste and the vapor phase in the innermost layer of confinement. Thus, the VOC concentration within the innermost confinement layer is constant.

4. A sufficient period of time has elapsed (i.e., the DAC has been satisfied) such that the VOC transport rates across all layers of confinement are equal and at steady-state. Thus, the VOC concentration within a void volume is constant and there is no accumulation of gas within any confinement layer.

5. The VOC concentration within a void volume is uniform at all times. Thus, there are no concentration variations within a single void volume.

6. Multiple layers of inner bags, liner bags, and SWB liners are treated as a single inner bag, liner bag, or SWB liner with a total thickness equal to the product of the number of such layers and the thickness of the individual layer.

7. The concentration of VOC outside the container is zero. Thus, there is rapid transport by diffusion and convection of VOC outside the container to maintain a zero concentration outside the drum.

8. All VOC properties and confinement layer properties are constant and uniform.

For the various layers of confinement that may be present in a container, the rate of VOC transport across each confinement layer, r, is defined as follows for each unique confinement layer:

6.1.1 Inner Bag (Twist and Tape)

Equation 1

$$r = \frac{\phi\, c\, \rho\, A_{ib} P}{n_{ib}\, x_{ib}} \Delta y_{ib} = \frac{K_{ib}}{n_{ib}} \Delta y_{ib}$$

where,

ϕ	=	76 T / (273.15 P) (dimensionless)
c	=	gas concentration at standard temperature (273.15 °K) and pressure (1 atm) from ideal gas law, P/RT (4.46×10^{-5} mol cm^{-3})
T	=	gas temperature (K)
ρ	=	VOC permeability [cm^3 (STP) cm^{-1} sec^{-1} $(cm\ Hg)^{-1}$ = 10^{10} Ba]
A_{ib}	=	surface area of inner bag (cm^2)
P	=	gas pressure (cm Hg)
n_{ib}	=	number of inner bags in packaging configuration
x_{ib}	=	thickness of inner bag (cm)
Δy_{ib}	=	VOC mole fraction difference across inner bag (dimensionless)
K_{ib}	=	inner bag VOC transport characteristic (mol sec^{-1})
R	=	gas constant (6236.6 cm Hg cm^3 mol^{-1} $°K^{-1}$)

6.1.2 Liner Bag (Twist and Tape)

Equation 2

$$r = \frac{\phi\, c\, \rho\, A_{lb} P}{n_{lb}\, x_{lb}} \Delta y_{lb} = \frac{K_{lb}}{n_{lb}} \Delta y_{lb}$$

where,

A_{lb}	=	surface area of liner bag (cm^2)
n_{lb}	=	number of liner bags in packaging configuration
x_{lb}	=	thickness of liner bag (cm)

Δy_{lb} = VOC mole fraction difference across liner bag (dimensionless)

K_{lb} = liner bag VOC transport characteristic (mol sec^{-1})

6.1.3 Inner Bag (Filtered)

Equation 3

$$r = \left(\frac{\phi\ c\ \rho\ A_{ib} P}{n_{ib}\ x_{ib}} + \frac{D^{*}_{VOC-bf}}{n_{ib}}\right) \Delta y_{ib} = \frac{K_{ib}}{n_{ib}} \Delta y_{ib}$$

where,

D^{*}_{VOC-bf} = VOC-bag filter diffusion characteristic (mol s^{-1}), defined in Equation 4:

Equation 4

$$D^{*}_{VOC-bf} = \frac{D_{VOC-air}}{D_{H_2-air}} D^{*}_{H_2-bf}$$

where,

$D_{VOC-air}$ = VOC diffusivity in air ($cm^2\ sec^{-1}$)

D_{H2-air} = Hydrogen diffusivity in air ($cm^2\ sec^{-1}$)

D^{*}_{H2-bf} = Hydrogen-bag filter diffusion characteristic (mol s^{-1}).

6.1.4 Liner Bag (Filtered)

Equation 5

$$r = \left(\frac{\phi\ c\ \rho\ A_{lb} P}{n_{lb}\ x_{lb}} + \frac{D^{*}_{VOC-bf}}{n_{lb}}\right) \Delta y_{lb} = \frac{K_{lb}}{n_{lb}} \Delta y_{lb}\ .$$

6.1.5 Rigid Drum Liner

Equation 6

$$r = \frac{P\ D_{VOC-air}\ A_{rl}}{R\ T\ x_{rl}}\ \Delta y_{rl} = K_{rl}\ \Delta y_{rl}$$

where,

A_{rl} = cross-sectional area of the hole in the rigid drum liner lid (cm^2)

x_{rl} = diffusional path length across hole in the rigid drum liner lid (cm)

Δy_{cl} = VOC mole fraction difference across the rigid liner (dimensionless)

K_{rl} = rigid liner transport characteristic (mol sec^{-1})

The VOC-diffusivity in air, $D_{VOC-air}$, can be estimated at low pressures using an equation developed from a combination of kinetic theory and corresponding-states arguments as:

Equation 7

$$D_{VOC-air} = 2.745 \times 10^{-4}\ \frac{T^{1.823}}{P}\ [p_{c-VOC}\ p_{c-air}]^{1/3}\ [T_{c-VOC}\ T_{c-air}]^{-1/2}\ [\frac{1}{M_{VOC}} + \frac{1}{M_{air}}]^{1/2}$$

where,

M_{VOC} = molecular weight of VOC (g/mol)

M_{air} = molecular weight of air = 29 g/mol

p_{c-VOC} = critical pressure of VOC (atm)

p_{c-air} = critical pressure of air = 36.4 atm

T_{c-VOC} = critical temperature of VOC (K)

T_{c-air} = critical temperature of air = 132 K.

6.1.6 SWB/Ten-Drum Overpack(TDOP)/Bin Liner (Fold and Tape)

Equation 8

$$r = \frac{c\ \rho\ A_{cl} P}{n_{cl}\ x_{cl}}\ \Delta y_{cl} = \frac{K_{cl}}{n_{cl}}\ \Delta y_{cl}$$

where,

A_{cl} = surface area of the container (i.e., SWB, TDOP, or Bin) liner bag (cm^2)

n_{ib} = number of container liner bags in packaging configuration

x_{cl} = thickness of the container liner bag (cm)

Δy_{cl} = VOC mole fraction difference across the container liner bag (dimensionless)

K_{cl} = container liner bag VOC transport characteristic (mol sec^{-1}).

6.1.7 SWB/TDOP/Bin Liner (Filtered)

Equation 9

$$r = \left(\frac{c\,\rho\,A_{cl}P}{n_{cl}\,x_{cl}} + \frac{D^{*}_{VOC-bf}}{n_{cl}}\right)\Delta y_{cl} = \frac{K_{cl}}{n_{cl}}\,\Delta y_{cl}$$

where all variables have been previously defined.

6.1.8 Container Filter

Equation 10

$$r = n_{cf}\;D^{*}_{VOC-cf}\;\Delta y_{cf} = n_{cf}\;D^{*}_{VOC-cf}\;y_{hs}$$

where,

Δy_{cf} = VOC mole fraction difference across the container filter (dimensionless)

y_{hs} = VOC mole fraction measured in container headspace (dimensionless)

n_{cf} = number of container filters in packaging configuration

D^{*}_{VOC-cf} = VOC-container filter diffusion characteristic (mol s^{-1}), calculated in Equation 11:

Equation 11

$$D^{*}_{VOC-cf} = \frac{D_{VOC-air}}{D_{H_2-air}}\,D^{*}_{H_2-cf}$$

where D^*_{H2-cf} is the container filter hydrogen diffusion characteristic (mol s^{-1}). Sequential substitution and rearrangement of terms yields a relationship for the innermost confinement layer VOC concentration as a function of the measured container headspace VOC concentration:

Equation 12

$$y_{icl} = y_{hs}\ [1 + n_{cf} D_{voc-cf} (\sum_{i=1}^{nl} \frac{n_i}{K_i})]$$

where,

y_{icl} = innermost confinement layer VOC mole fraction

n_i = number of type "i" confinement layers in packaging configuration

K_i = transport characteristic of type "i" confinement layer (mol s^{-1})

nl = number of different confinement layer types.

Multiplying both sides of Equation 12 by a conversion factor (10^6 ppm/mole fraction) yields the following final equation for the prediction factor.

Equation 13

$$Y_{icl} = Y_{hs}\ [1 + n_{cf} D_{voc-cf} (\sum_{i=1}^{nl} \frac{n_i}{K_i})]$$

where,

Y_{icl} = innermost confinement layer VOC concentration (ppm)

Y_{hs} = measured VOC concentration in container headspace (ppm)

Thus, the prediction factor, PF, is defined as:

Equation 14

$$PF = [1 + n_{cf} D_{voc-cf} (\sum_{i=1}^{nl} \frac{n_i}{K_i})]$$

7. DISCUSSION

The calculation of DACs for three common drum venting and sampling scenarios provides more realistic waiting periods for sampling than current conservative DACs applied uniformly to all packaging configurations. For example, DAC_2 values indicate that unvented drums that have been in storage in excess of DAC_1 values can be realistically sampled in anywhere from 4 to 36 days depending on the liner lid opening and drum filter vent installed at the time of venting. This could provide relief of over 200 days in some cases in reducing the waiting time required before sampling the drum headspace.

A comparison of DAC_2 values calculated for drums with 0.375-in diameter opening in liner lid and a drum vent with a hydrogen diffusion characteristic of 3.7×10^{-6} mol/s/mol fr (20 and 25 days) to similar values reported by Connolly et al. (1998) (18 and 22 days) show close agreement. The higher values calculated in this report result from more restrictive packaging (S5000 waste or Waste Types II and III), an assumption of a filter vent with 10% lower diffusion characteristic, and a model assumption of a 10% lower drum liner headspace concentration at the time of venting. The DAC for newly packaged and vented waste drums with a packaging configuration for Waste Types II and III was previously calculated to be 142 days (Connolly et al., 1998). This value is not in Table 4 because its packaging configuration was assumed to have three inner bags, two liner bags, and filter vent with an average hydrogen diffusion characteristic of 4.2×10^{-6} mol/s/mol fr. Some DAC_3 values are greater than earlier DAC values of 142 and 225 days (Connolly et al., 1998). The higher DAC_3 values result from assuming the limiting values for the filter vent diffusion characteristic and the liner lid opening as well as considering a greater possible number of polymer bags in the drum.

Separate DAC_3 values were calculated for S3000/S4000 (Waste Types I and IV) and S5000 (Waste Types II and III) waste packaging configurations. Since waste packaging configurations were assumed for each waste type, these DACs should be considered packaging-specific DACs and not waste-specific. In some cases, S3000/S4000 (Waste Types I and IV) waste is packaged inside inner bags before being placed inside a liner bag. An argument can be made that the S5000 (Waste Types II and III) DAC_3 value for the appropriate packaging configuration could be used to define when a headspace gas sample can be taken. In this case, a comparison of DAC_3 values by waste type for a given packaging configuration shows that S3000/S4000 (Waste Types I and IV) DAC_3 values are higher and, thus, more conservative.

The DAC values calculated for the SWBs and the pipe component are intended to conservatively bound the wide range of likely packaging configurations. As more information becomes available on the configurations used, it is foreseeable that additional packaging-specific DACs could be generated in the same manner as was for waste drums in this report. The VOC concentration multiplier was defined to relate the measured VOC concentration in the headspace of a waste drum containing a vented pipe component (i.e. pipe overpack) or metal can to the VOC headspace concentration when it had achieved 90% of it's steady-state value. This approach was developed to avoid excessively lengthy waiting times due to slow diffusion of the VOCs.

8. REFERENCES

Connolly, M.J., S.M. Djordjevic, K.J. Liekhus, C.A. Loehr, and L.R. Spangler, June 1998, "Position for Determining Gas Phase Volatile Organic Compound Concentrations in Transuranic Waste Containers," *INEEL-95/0109*, Rev. 2, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho.

Liekhus, K.J., S.M. Djordjevic, M. Devarakonda, and M.J. Connolly, 1999, "Determination of Transuranic Waste Container Drum Age Criteria and Prediction Factors Based on Packaging Configurations," *INEEL/EXT-99-01010*, Bechtel BWXT Idaho, LLC, Idaho Falls, Idaho.

Liekhus K.J. and A.G. Chambers, 2000, "Software Validation and Verification of Revised Computer Code (VDRUM) Used to Calculate Drum Age Criteria", *INEEL/EXT-2000-01208*, Bechtel BWXT Idaho, LLC, Idaho Falls, Idaho.

Appendix A

Model Input Parameters to Calculate DAC

The physical properties of indicator VOCs used in calculating DACs are listed in Table A-1. Toluene, 1,1-dichloroethene (DCE), or methyl isobutyl ketone (MIBK) have been identified as the VOCs that yield the highest packaging-specific DACs (Connolly et al., 1998). Toluene defined the DAC in drums containing drum liners during transient conditions where the VOC solubility in the drum liner is important. In cases where the VOC concentration in the liner had approached its equilibrium concentration or in drums that did not contain a drum liner, the time required for the other two VOCs to reach near equilibrium concentration define the DAC. The diffusivity of DCE and MIBK in air is estimated using the VOC critical properties.

Table A-1. VOC physical properties used to calculate DAC_2 values.

VOC	MW	P_{voc}	D_{voc}	T_c	P_c	H	k
Toluene	92.1	669e-10	0.0849	591.8	40.5	0.002857	7.e-6
DCE	96.9	110e-10	0	513.0	47.5	0.09091	8.e-6
MIBK	100.2	130e-10	0	571.0	32.3	0.01724	8.e-6

MW – molecular weight

P_{voc} – VOC permeability across polymer bags, cm^3(STP) cm cm^{-2} s^{-1} (cm Hg)$^{-1}$

D_{voc} – VOC diffusivity in air, cm^3 s^{-1}

T_c – critical temperature, K

P_c – critical pressure, atm

H – VOC Henrys constant for drum liner, cm^3 polymer atm cm^{-3} (STP)

k – VOC mass transfer coefficient at drum liner, s^{-1}

DAC_1 Model Input Parameters

The physical dimensions of each layer of confinement in waste drums containing S3000/S4000 and S5000 drums specified in the model input file are listed in Table A-2. Since accumulating VOC will interact with the drum liner, toluene is the chosen VOC to achieve the highest DAC. The initial VOC concentration profile has a constant VOC concentration within the innermost layer of confinement and zero in all other layers indicative of a newly packaged drum. The drum is unvented so the diffusion characteristic of the filter vent is set to zero. All drums are assumed to be at 25°C and ambient pressure of 76 cm Hg (1 atm).

Table A-2. Physical parameters used to calculate DAC_1 values

Layer of Confinement	A_p (cm^2)	V (cm^3)	x_p (cm)
Inner bags (S5000 only)	14,000	---	0.050
Liner Bags (S3000/S4000) Liner Bags (S5000)	3,000 14,000	20,000	0.056
Drum Liner	15,500	40,000	0.229
Drum Headspace	---	28,000	---

A_p – permeable/soluble surface area

V – void volume inside later of confinement

x_p - thickness of permeable/soluble polymer

DAC_2 Model Input Parameters

The methodology for calculating the drum age criterion in a drum being vented after remaining unvented for at least DAC_1 days is the same as for newly vented drums with liners at complete equilibrium. The only difference is in calculating DAC_2 values, the VOC in the drum liner headspace is assumed to be at 90% of the VOC concentration within the innermost layer of confinement instead of 100%. The VOC solubility in the liner is not considered since it assumed that the liner is nearly saturated. This is reflected in the model input file by setting the mass-transfer coefficients (k) for each VOC to zero. All other VOC physical properties used to calculated DAC_2 values are listed in Table A-1. The physical parameters used to calculate DAC_2 values are listed in Table A-2. All drums are assumed to be at 25°C and ambient pressure of 76 cm Hg (1 atm). The other variables considered in calculating the DAC_2 values were the diameter of the circular opening in the drum liner lid and the hydrogen diffusion characteristic of the drum filter vent. The cross-sectional areas and diffusion lengths associated with each liner lid opening is shown in Table A-3. **The drum filter vent H_2 diffusion characteristic (mol/s/mol fr.) was evaluated at three values: 1.9×10^{-6} ; 3.7×10^{-6} ; 3.7×10^{-5} .**

Table A-3. Physical parameters associated with liner lid opening

Liner Lid Opening Diameter (in)	A_d (cm^2)	x_d (cm)
0.30	0.456	1.2
0.375	0.71	1.2
0.75	2.85	1.4
1.0	5.08	1.4

A_d – diffusion cross-sectional area

x_d - diffusional length

The initial concentration is defined by a constant VOC concentration within the innermost layer of confinement, with the same VOC concentration is all other layers of confinement except the drum liner headspace which is assumed to have achieved 90% of the constant source concentration. The drum headspace is assumed to be free of any VOCs until the liner is puncture. This is a conservative assumption.

DAC_3 Model Input Parameters

Three packaging configurations in waste drums were considered for each waste type (S3000/S4000 and S5000). The packaging configurations are distinguished by the number of bags and were selected to cover the range of packaging configurations. The physical parameters associated with each packaging configuration is summarized in Table A-4. The liner lid opening of five different sizes as well as the case of no liner present in the waste drum were considered. The physical properties associated with the liner in each case is listed in Table A-5. **The drum filter vent H_2 diffusion characteristic (mol/s/mol fr.) was evaluated at three values: 1.9×10^{-6} ; 3.7×10^{-6} ; 3.7×10^{-5} .** The VOCs and their physical properties used in calculating DAC_3 values are listed in Table A-1.

Table A-4. Physical parameters associated with waste type and packaging configuration.

		Inner bag		Liner Bag	
Waste Type	Packaging Configuration	A_p (cm^2)	x_p (cm)	A_p(cm^2)	x_p (cm)
S3000/S4000	1: No liner bags	---	---	3,000	0.0005*
S3000/S4000	2: One liner bag	---	---	3,000	0.028
S3000/S4000	3: Two liner bags	---	---	3,000	0.056
S5000	1: No inner or liner bags	---	---	14,000	0.0003*
S5000	2: Three inner, one liner bags	14,000	0.038	14,000	0.028
S5000	3: Four inner, two liner bags	14,000	0.050	14,000	0.056

*Model requires one bag so bag thickness is assumed to be negligible.

Table A-5. Physical parameters associated with liner and liner lid for DAC_3.

Liner lid opening diameter (in)/liner status	$A_{d,opening}$ (cm^2)	$x_{d,opening}$ (cm)	$A_{p,liner}$(cm^2)	$x_{p,liner}$ (cm)
0.3	0.456	1.2	15,500	0.229
0.375	0.71	1.2	15,500	0.229
0.75	2.85	1.4	15,500	0.229
1.0	5.08	1.4	15,500	0.229
No lid	150^	1.4	12,800	0.229
No liner	150^	1.4	12,800	0.00005*

^Larger values cause instability in program and do not yield a lower DAC.

*Represent liner as having negligible thickness

In addition, two packaging configurations for standard waste boxes (SWBs) and a bounding case of bagged waste inside a vented metal can inside a vented pipe component were evaluated. The SWB packing configuration 1 assumes waste wrapped inside 5 inner bags is placed in a single liner bag in a SWB. The SWB packaging configuration 2 assumes waste is directly placed inside a single liner bag in a SWB. For the two cases of SWBs, the DAC was defined by the physical properties of DCE (see Table A-1). The SWB has one or more filter vents with a total hydrogen diffusion characteristic of 7.4×10^{-6} mol/s/mol fr. The initial concentration profiles in all configurations is a constant VOC concentration inside the innermost layer of confinement and zero in all other layers indicative of a newly packaged container. The physical dimensions of each layer of confinement for the SWBs and pipe component used as model input are listed in Table A-6. The code VDRUM.FOR was used to calculate the DACs for the SWBs. The code VDRUM2.FOR was used to calculate the DAC for the limiting packaging configuration for a pipe component.

Table A-6. Model input parameters for calculating SWB and pipe component DACs.

Packaging Configuration	Layer of confinement	Ap (cm^2)	x_p (cm)	V (cm^3)	A_d (cm^2)	x_d (cm)	D*, mol/s/mol
SWB	Inner bag (case 2 only)	14,000	0.063	---	---	---	---
	Liner Bag	14,000	0.036	190,000	---	---	---
	Liner (none)*	14,000	0.0001*	100,000	150*	1.4	---
	SWB Headspace	---	---	100,000	---	---	7.4e-6
Pipe component	Inner bags	500	---	---	0.025	---	---
	Metal can	---	---	1,000	---	---	1.9e-6
	Pipe component	---	---	46,000	---	---	1.9e-6

* - Liner wall thickness is assumed negligible to mimic configuration with no liner.

Appendix B

Model Input Parameters to Calculate VOC Concentration Multipliers

The physical properties of VOCs used in calculating VOC concentration multipliers are listed in Table B-1. The VOC diffusivity, in some cases, is estimated using the VOC critical properties.

Table B-1. VOC physical properties used to calculate VOC concentration multipliers.

VOC	MW	P_{voc}	D_{voc}	T_c	P_c	H	k
Carbon tetrachloride	153.82	193e-10	0.0828	556.4	45.0	0.0217	6.e-5
Cyclohexane	84.1	12.4e-10	0	553.2	40.2	0.8333	3.e-5
Methanol	32.0	135e-10	0.152	513.2	78.5	0.0272	2.4e-7
Dichloromethane	84.9	263e-10	0.104	510.0	62.2	0.0431	2.e-6
Toluene	92.1	669e-10	0.0849	591.8	40.5	0.002857	7.e-6
Trichloroethane	133.4	143e-10	0.0794	545.0	42.4	0.0402	1.e-5
Trichloroethylene	131.4	583e-10	0.0875	572.0	49.8	0.00640	6.e-5
Freon-13	187.4	38.6e-10	0	487.3	33.7	0.1973	1.e-5
p-xylene	106.2	811e-10	0.0670	616.7	34.8	0.00147	4.e-6
Acetone	58.1	150e-10	0	508.1	46.4	0.06667	8.e-6
Butanol	74.1	300e-10	0	563.1	43.6	0.02273	8.e-6
Chloroform	119.4	260e-10	0	536.4	53.0	0.04545	8.e-6
1,1-dichloroethene	96.9	110e-10	0	513.0	47.5	0.09091	8.e-6
Methyl ethyl ketone	72.1	165e-10	0	536.8	41.5	0.03704	8.e-6
Methyl isobutyl ketone	100.2	130e-10	0	571.0	32.3	0.01724	8.e-6
1,1,2,2-tetrachloroethane	167.9	2300e-10	0	661.2	57.6	0.003846	8.e-6
Tetrachloroethene	165.8	610e-10	0	620.2	47.0	0.009091	8.e-6
Benzene	78.1	280e-10	0	562.2	48.3	0.02941	8.e-6
Bromoform	252.7	4800e-10	0	658.7	69.2	0.00303	8.e-6
Chlorobenzene	112.6	600e-10	0	632.4	44.6	0.007692	8.e-6
1,1-dichloroethane	99.0	200e-10	0	523.0	50.0	0.05556	8.e-6
1,2-dichloroethane	99.0	445e-10	0	566.0	53.0	0.02381	8.e-6
Cis-1,2-dichloroethene	96.9	295e-10	0	537.0	55.3	0.04545	8.e-6
Ethylbenzene	106.2	260e-10	0	617.2	35.5	0.00833	8.e-6
Ethyl ether	74.1	40e-10	0	466.7	35.9	0.14706	8.e-6
1,3,5-trimethylbenzene	120.2	260e-10	0	637.3	30.9	0.004762	8.e-6
1,2,4-trimethylbenzene	120.2	320e-10	0	649.2	31.9	0.0040	8.e-6
o-xylene	106.2	360e-10	0	630.3	36.8	0.006667	8.e-6
m-xylene	106.2	260e-10	0	617.1	34.9	0.0083333	8.e-6

MW – molecular weight

P_{voc} – VOC permeability across polymer bags, cm^3(STP) cm cm^{-2} s^{-1} (cm Hg)$^{-1}$

D_{voc} – VOC diffusivity in air, cm^3 s^{-1}

T_c – critical temperature, K

P_c – critical pressure, atm

H – VOC Henrys constant for drum liner, cm^3 polymer atm cm^{-3} (STP)

k – VOC mass transfer coefficient at drum liner, s^{-1}

Three packaging configurations have been identified as bounding cases for waste stored in a pipe component. The three configurations and the other configurations bounded by them are listed below:

Packaging Configuration 1: 2 Inner Bags (IB)-Pipe component (PC)-Drum Liner (DL)-Vented Drum (DF)

Packaging Configuration Subset: 2 Filtered Inner Bags (FIB)-PC-DL-DF

Packaging Configuration 2: 2IB-Vented Can (FC)-PC-DL-DF

Packaging Configuration Subset:
- FC-2FIB-FC-Filtered Liner Bag (FLB)-DL-DF
- FC-2FIB-FC-2FLB-DL-DF
- 2FIB-FC-PC-DL-DF

Packaging Configuration 3: 3IB-FC-2 Liner Bags (LB)-DL-DF

Packaging Configuration Subset:
- 2FIB-FC-FIB-FLB-DL-DF
- 2FIB-FC-FLB-DL-DF
- FIB-FC-FLB-DL-DF
- 3FIB-FC-FIB-FLB-DL-DF
- 2IB-FC-IB-LB-DL-DF
- 3IB-FC-IB-LB-DL-DF
- 2IB-FC-LB-DL-DF
- 2FIB-FC-2FLB-DL-DF

Filtered bags offer considerably less resistance to VOC transport across polymer bags than unfiltered bags. That is why in Packaging Configuration 2 configurations containing up to four layers of vented bags are in the subset below the bounding case contain fewer unfiltered bags. Drum liners holding pipe components are assumed to have no lids. The physical dimensions assumed for these packaging configurations are tabulated in Table B-2.

The initial concentration profiles in all configurations is a constant VOC concentration inside the innermost layer of confinement and zero in all other layers indicative of a newly packaged container.

The filter vent on the metal can and pipe component as well as the filter vent on the drum lid are assumed to have a hydrogen diffusion characteristic of one of two values: 1.9e-6 mol/s/mol fr and 3.7e-6 mol/s/mol fr.

The VOC concentration multipliers are calculated in each packaging configuration after a specific period of time. Four time periods were selected: 75, 150, 300, and 600 days.

Table B-2. Physical dimensions used to calculate VOC concentration multipliers in Tables 6 through 9.

Packaging Configuration	Layer of confinement	A_p, cm^2	x_p, cm	V, cm^3	A_d, cm^2	x_d, cm
2IB-PC-DL-DF (Case 1)	Inner Bags	1,000	0.025	---	---	---
	Pipe component	---	---	45,000	---	---
	Drum Liner	12,800	0.279	105,000	150	1.4
	Drum Headspace	---	---	18,000	---	---
2IB-FC-PC-DL-DF (Case 2)	Inner Bags	500	0.025	---	---	---
	Vented Can	---	---	1,000	---	---
	Pipe component	---	---	46,000	---	---
	Drum Liner	12,800	0.279	105,000	150.	1.4
	Drum Headspace	---	---	18,000	---	---
3IB-FC-2LB-DL-DF (Case 3)	Inner Bags	500	0.038	---	---	---
	Vented Can	---	---	1,000	---	---
	Liner Bags	4,000	0.075	37,000	---	---
	Drum Liner	15,500	0.279	134,000	2.85	1.2
	Drum Headspace	---	---	18,000	---	---
A_p – permeable/soluble surface area						
x_p - thickness of permeable/soluble polymer						
V – void volume inside later of confinement						
A_d – diffusion cross-sectional area						
x_d - diffusional length						

Software Validation and Verification of Revised Computer Code (VDRUM) Used to Calculate Drum Age Criteria INEEL/EXT-2000-01208

Appendix B

Appendix B

The output from VDRUM2 is compared to output from VDRUM1 identical waste packaging configurations and packaging scenarios. Two waste packaging configurations are evaluated. One configuration consists of a vented drum, drum liner, polymer liner bags, and small polymer bags surrounding the waste as seen in drums containing in Type II (inorganic solids) and Type III (organic solids) waste. The other configuration considered consists of a vented drum, drum liner, and polymer liner bags in which waste is placed as seen in drums containing Type I (inorganic solidified) and Type IV (organic solidified) waste. The input/output files for each case are summarized in Table B-1.

Table B-1. Summary of input/output files for each DAC-calculating program.

	VDRUM1	VDRUM2
Waste Type II/III	vbase/vbase.out	zbaseii/zbaseii.out
Waste Type I/IV	rbase/rbase.out	zbaseiv/zbaseiv.out

The content of the input and output files are listed on the following pages. In the case of VDRUM1 output, the first number listed after the name of the volatile organic compound (VOC) is the DAC value, or the number of days that are required for the drum headspace to achieve 90% of the steady-state concentration. The two numbers after the DAC value are the 90% of steady-state and steady-state VOC concentrations, respectively. Similar values are displayed in output files from VDRUM2 but are labeled more clearly. An additional number is displayed in VDRUM2 output. This number is the ratio of the 90% of steady-state VOC concentration to the VOC concentration achieved at the DAC value. In these cases, the ratio should equal unity.

INPUT FILE (VBASE) to VDRUM.FOR
baseline for Waste Types II/III, 12 VOCs considered
newly packaged, vented 55-gal waste drums
all parameters defined in INEL-95/0109, Rev. 2

```
'vbase','vbase.out',12
'carbon tetrachloride',1000.,0.,0.,0.
153.82,193.e-10,0.0828,0.,0.,3.03e-7,0.0217,6.e-5,0.
'methanol',1000.,0.,0.,0.
32.0,135.e-10,0.152,0.,0.,6.05e-7,0.0272,2.4e-7,0.
'dichloromethane',1000.,0.,0.,0.
84.9,263.e-10,0.104,0.,0.,4.43e-7,0.0431,2.e-6,0.
'toluene',1000.,0.,0.,0.
92.1,669.e-10,0.0849,0.,0.,3.66e-7,0.002857,7.e-6,0.
'trichloroethylene',1000.,0.,0.,0.
131.4,583.e-10,0.0875,0.,0.,3.2e-7,0.00640,6.e-5,0.
'butanol',1000.,0.,0.,0.
74.1,300.e-10,0.,563.1,43.6,0.,0.02273,8.e-6,0.
'chloroform',1000.,0.,0.,0.
119.4,260.e-10,0.,536.4,53.0,0.,0.04545,8.e-6,0.
'1,1-dichloroethene',1000.,0.,0.,0.
96.9,110.e-10.0.,513.0,47.5,0.,0.09091,8.e-6,0.
'methyl ethyl ketone',1000.,0.,0.,0.
72.1,165.e-10,0.,536.8,41.5,0.,0.03704,8.e-6,0.
'methyl isobutyl ketone',1000.,0.,0.,0.
100.2,130.e-10,0.,571.0,32.3,0.,0.01724,8.e-6,0.
'1,1,2,2-tetrachloroethane',1000.,0.,0.,0.
167.9,2300.e-10,0.,661.2,57.6,0.,0.003846,8.e-6,0.
'chlorobenzene',1000.,0.,0.,0.
112.6,600.e-10,0.,632.4,44.6,0.,0.007692,8.e-6,0.
14000.,0.,0.,0.038,0.
14000.,0.,20000.,0.056,0.
15500.,0.71,40000.,0.229,1.2
0.,0.,28000.,0.,0.
25.,76.,42.e-7

c baseline for Waste Types II/III, 12 VOCs considered
c newly packaged, vented 55-gal waste drums
c all parameters defined in INEL-95/0109, Rev. 2
```

OUTPUT FILE (VBASE.OUT) FROM VDRUM.FOR (INPUT FILE = VBASE)

```
vbase
carbon tetrachloride          51  762.5723    845.3864
methanol                      64  718.2869    797.6616
dichloromethane               32  744.8869    826.5574
toluene                      142  752.3510    835.4522
trichloroethylene             74  773.9573    858.1149
butanol                       40  717.7332    793.4727
chloroform                    29  714.6116    789.9650
1,1-dichloroethene            32  684.3615    759.8938
methyl ethyl ketone           39  701.5074    777.8983
methyl isobutyl ketone        76  699.6860    774.9249
1,1,2,2-tetrachloroethane     81  725.5580    803.9965
chlorobenzene                 68  724.5751    803.2201
```

INPUT FILE (RBASE) to VDRUM.FOR
baseline for Waste Types I/IV, 12 VOCs considered
newly packaged, vented 55-gal waste drums
all parameters defined in INEL-95/0109, Rev. 2

```
'rbase','rbase.out',12
'carbon tetrachloride',0.,1000.,0.,0.
153.82,193.e-10,0.0828,0.,0.,3.03e-7,0.0217,6.e-5,0.
'methanol',0.,1000.,0.,0.
32.0,135.e-10,0.152,0.,0.,6.05e-7,0.0272,2.4e-7,0.
'dichloromethane',0.,1000.,0.,0.
84.9,263.e-10,0.104,0.,0.,4.43e-7,0.0431,2.e-6,0.
'toluene',0.,1000.,0.,0.
92.1,669.e-10,0.0849,0.,0.,3.66e-7,0.002857,7.e-6,0.
'trichloroethylene',0.,1000.,0.,0.
131.4,583.e-10,0.0875,0.,0.,3.2e-7,0.00640,6.e-5,0.
'butanol',0.,1000.,0.,0.
74.1,300.e-10,0.,563.1,43.6,0.,0.02273,8.e-6,0.
'chloroform',0.,1000.,0.,0.
119.4,260.e-10,0.,536.4,53.0,0.,0.04545,8.e-6,0.
'1,1-dichloroethene',0.,1000.,0.,0.
96.9,110.e-10,0.,513.0,47.5,0.,0.09091,8.e-6,0.
'methyl ethyl ketone',0.,1000.,0.,0.
72.1,165.e-10,0.,536.8,41.5,0.,0.03704,8.e-6,0.
'methyl isobutyl ketone',0.,1000.,0.,0.
100.2,130.e-10,0.,571.0,32.3,0.,0.01724,8.e-6,0.
'1,1,2,2-tetrachloroethane',0.,1000.,0.,0.
167.9,2300.e-10,0.,661.2,57.6,0.,0.003846,8.e-6,0.
'chlorobenzene',0.,1000.,0.,0.
112.6,600.e-10,0.,632.4,44.6,0.,0.007692,8.e-6,0.
0.,0.,0.,0.,0.
3000.,0.,20000.,0.056,0.
15500.,0.71,40000.,0.229,1.2
0.,0.,28000.,0.,0.
25.,76.,42.e-7
```

c baseline for Waste Types I/IV, 12 VOCs considered
c newly packaged, vented 55-gal waste drums
c all parameters defined in INEL-95/0109, Rev. 2

OUTPUT FILE (RBASE.OUT) FROM VDRUM.FOR (INPUT FILE = RBASE)

rbase

carbon tetrachloride	92	726.7985	807.4005
methanol	115	638.3188	708.3283
dichloromethane	50	710.7165	787.7477
toluene	225	738.7659	820.7675
trichloroethylene	119	759.8959	843.3984
butanol	65	686.6910	760.4871
chloroform	46	677.4800	751.3829
1,1-dichloroethene	57	613.2073	680.0746
methyl ethyl ketone	68	649.6926	721.7274
methyl isobutyl ketone	140	644.1774	714.7215
1,1,2,2-tetrachloroethane	100	716.8054	795.3849
chlorobenzene	104	710.4477	787.3361

INPUT FILE (ZBASEII) to VDRUM2.FOR

This is an input file for the program vdrum2.for. Duplication of vbase (input file for vdrum.for)

```
'zbaseii','zbaseii.out'
12,4,1
'carbon tetrachloride',1000.,0.,0.,0.
153.82,193.e-10,0.0828,556.4,45.0,0.0217,6.e-5
'methanol',1000.,0.,0.,0.
32.0,135.e-10,0.152,513.2,78.5,0.0272,2.4e-7
'dichloromethane',1000.,0.,0.,0.
84.9,263.e-10,0.104,510.,62.2,0.0431,2.e-6
'toluene',1000.,0.,0.,0.
92.1,669.e-10,0.0849,594.0,41.6,0.002857,7.e-6
'trichloroethylene',1000.,0.,0.,0.
131.4,583.e-10,0.0875,572.0,49.8,0.00640,6.e-5
'butanol',1000.,0.,0.,0.
74.1,300.e-10,0.,563.1,43.6,0.02273,8.e-6
'chloroform',1000.,0.,0.,0.
119.4,260.e-10,0.,536.4,53.0,0.04545,8.e-6
'1,1-dichloroethene',1000.,0.,0.,0.
96.9,110.e-10,0.,513.0,47.5,0.09091,8.e-6
'methyl ethyl ketone',1000.,0.,0.,0.
72.1,165.e-10,0.,536.8,41.5,0.03704,8.e-6
'methyl isobutyl ketone',1000.,0.,0.,0.
100.2,130.e-10,0.,571.0,32.3,0.01724,8.e-6
'1,1,2,2-tetrachloroethane',1000.,0.,0.,0.
167.9,2300.e-10,0.,661.2,57.6,0.003846,8.e-6
'chlorobenzene',1000.,0.,0.,0.
112.6,600.e-10,0.,632.4,44.6,0.007692,8.e-6
14000.,0.,0.,0.038,0.,0.
14000.,0.,20000.,0.056,0.,0.
15500.,0.71,40000.,0.229,1.2,0.
0.,0.,28000.,0.,0.,42.e-7
25.,76.,0.9,990
```

OUTPUT FILE (ZBASEII.OUT) FROM VDRUM2.FOR (INPUT FILE = ZBASEII)

zbaseii

	N(days)	[ ]@N	[ ]@SS	0.9[ ]SS/[ ]N
carbon tetrachloride	48	713.64	792.75	1.0
methanol	63	699.13	775.99	1.0
dichloromethane	32	723.17	797.54	1.0
toluene	142	737.40	818.00	1.0
trichloroethylene	71	735.64	814.71	1.0
butanol	40	717.73	793.89	1.0
chloroform	29	714.61	790.21	1.0
1,1-dichloroethene	32	684.36	760.00	1.0
methyl ethyl ketone	39	701.51	778.08	1.0
methyl isobutyl ketone	76	699.69	775.19	1.0
1,1,2,2-tetrachloroethane	83	730.44	811.16	1.0
chlorobenzene	68	724.58	804.58	1.0

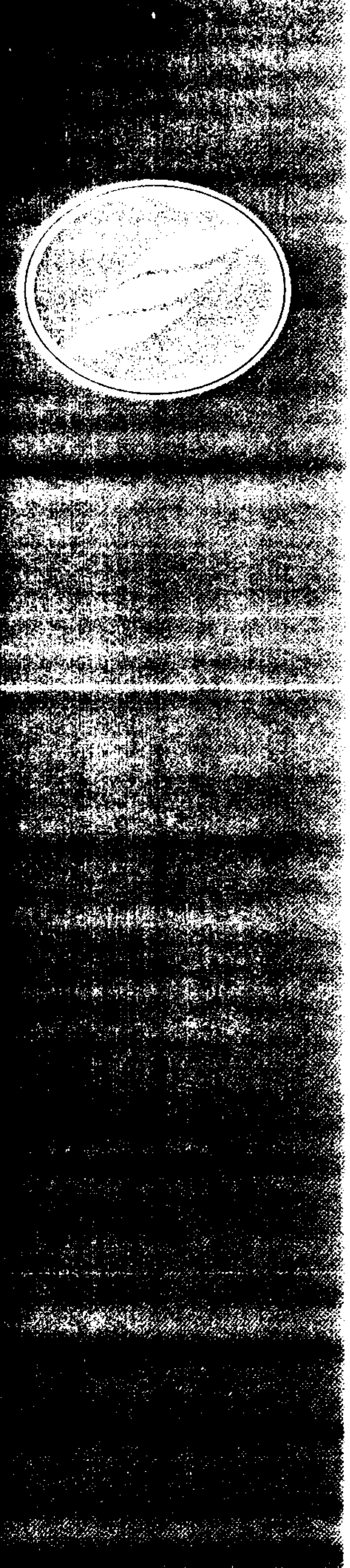
INPUT FILE (ZBASEIV) to VDRUM2.FOR
This is an input file to vdrum2.for. Duplication of rbase (an input file for vdrum.for)

```
'zbaseIV','zbaseIV.out'
12,3,1
'carbon tetrachloride',1000.,0.,0.
153.82,193.e-10,0.0828,556.4,45.0,0.0217,6.e-5
'methanol',1000.,0.,0.
32.0,135.e-10,0.152,513.2,78.5,0.0272,2.4e-7
'dichloromethane',1000.,0.,0.
84.9,263.e-10,0.104,510.,62.2,0.0431,2.e-6
'toluene',1000.,0.,0.
92.1,669.e-10,0.0849,594.0,41.6,0.002857,7.e-6
'trichloroethylene',1000.,0.,0.
131.4,583.e-10,0.0875,572.0,49.8,0.00640,6.e-5
'butanol',1000.,0.,0.
74.1,300.e-10,0.,563.1,43.6,0.02273,8.e-6
'chloroform',1000.,0.,0.
119.4,260.e-10,0.,536.4,53.0,0.04545,8.e-6
'1,1-dichloroethene',1000.,0.,0.
96.9,110.e-10,0.,513.0,47.5,0.09091,8.e-6
'methyl ethyl ketone',1000.,0.,0.
72.1,165.e-10,0.,536.8,41.5,0.03704,8.e-6
'methyl isobutyl ketone',1000.,0.,0.
100.2,130.e-10,0.,571.0,32.3,0.01724,8.e-6
'1,1,2,2-tetrachloroethane',1000.,0.,0.
167.9,2300.e-10,0.,661.2,57.6,0.003846,8.e-6
'chlorobenzene',1000.,0.,0.
112.6,600.e-10,0.,632.4,44.6,0.007692,8.e-6
3000.,0.,20000.,0.056,0.,0.
15500.,0.71,40000.,0.229,1.2,0.
0.,0.,28000.,0.,0.,42.e-7
25.,76.,0.9,0
```

OUTPUT FILE (ZBASEIV.OUT) FROM VDRUM2.FOR (INPUT FILE = ZBASEIV)

zbaseIV

	N(days)	[ ]@N	[ ]@SS	0.9[ ]SS/[ ]N
carbon tetrachloride	87	672.01	745.84	1.0
methanol	112	613.43	680.86	1.0
dichloromethane	49	682.01	754.24	1.0
toluene	226	723.06	803.09	1.0
trichloroethylene	115	719.01	797.08	1.0
butanol	65	686.69	761.07	1.0
chloroform	46	677.48	751.73	1.0
1,1-dichloroethene	57	613.21	680.21	1.0
methyl ethyl ketone	69	652.31	721.97	1.0
methyl isobutyl ketone	140	644.18	715.08	1.0
1,1,2,2-tetrachloroethane	105	726.57	806.85	1.0
chlorobenzene	104	710.47	788.99	1.0



Idaho National Engineering and Environmental Laboratory

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Software Validation and Verification of Revised Computer Code (VDRUM) Used to Calculate Drum Age Criteria

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CONTENTS

Software Validation and Verification of Revision of Computer Code (VDRUM) Used to Calculate Drum Age Criteria

1. BACKGROUND

In 1995, software written in the FORTRAN language was developed, validated, and used to estimate the time required for the volatile organic compound (VOC) concentration in a waste drum to reach near steady-state or equilibrium conditions. The name of the program was VDRUM.FOR, Revision 1 (referred to from now on as VDRUM1). The calculated time is referred to as the drum age criterion (DAC). The verification and the validation of the software to predict time-dependent concentrations in vented waste drums was conducted using experimental data and results from previously validated software.[1] The software was used to determine the DAC for two broad categories of waste packaging configurations under three different scenarios. The two waste packaging configurations considered were:

1. Waste drum, rigid drum liner, and polymer liner bags in which waste is placed;
2. Waste drum, rigid liner, polymer liner bags, and small polymer bags in which waste is placed.

The packaging scenarios considered included:

1. Previously packaged waste drums, newly vented;
2. Newly packaged, vented waste drums;
3. Newly packaged, unvented waste drums.

The waste packaging configurations and packaging scenarios selected were intended to serve as bounding, or limiting, cases representing the most conservative estimate for a DAC applicable to all similarly packaged waste drums.[2] However, given the wide variety of waste packaging variables (total layers of polymer bags, as well as the presence or absence of bag filters, drum liner, and vented metal cans), there is a need for calculating packaging-specific DACs that would reflect more accurate, and possibly less restrictive, minimum vent times.

2. CHANGE REQUEST DESCRIPTION AND JUSTIFICATION

The software is modified to allow calculations of DAC values for a wider range of waste drum packaging configurations. The modifications will enable the user to calculate DACs for waste drums with three to six layers of confinement, allow for the presence of vented layers of confinement, and enable the user to calculate the time to achieve a user-specified percentage of the steady-state drum headspace concentration or calculate the drum headspace concentration after a user-specified period of time.

The code no longer considers the possibility of gas generation in the waste drum. This feature was useful in modeling hydrogen generation in the drum. In addition, the capability of the code to model newly packaged, unvented drum and drum liner was removed. The code VDRUM1 was used to determine the DAC for three different packaging scenarios. The results demonstrated that the most conservative packaging scenario is newly packaged, vented waste drums. The DAC values for this scenario were applied to all other packaging scenarios. It is assumed new DAC values calculated for other packaging configurations will be for newly packaged, vented waste drums.

3. SOFTWARE QUALITY ASSURANCE PLAN

The software quality assurance described in this document is designed to meet the intent of the specifications described in NQA-2 Part 2.7. Model equations, the original computer code, and the revision to the computer code were developed by Dr. Kevin Liekhus at the Idaho National Engineering and Environmental Laboratory (INEEL). Dr. Liekhus has a Ph.D in chemical engineering and extensive experience in modeling transport phenomena.[3] This document and model verifications were reviewed by Andrea Chambers at the INEEL. Ms. Chambers has an undergraduate degree in chemical engineering.

4. SOFTWARE REQUIREMENTS

The functionality and design requirements of the VDRUM1 were defined in the validation documentation.[1] These requirements that are applicable to a revised VDRUM1 include (a) prompting the user to specify the input data file defining user-specified initial values and model parameters; (b) reading the input data file; (c) defining additional variables in terms of user-specified input; (d) solving a series of ordinary differential equations to define the change in gas concentration within each layer of confinement as a function of time; (e) calculating equilibrium or steady-state concentration; (f) calculating the time to reach the DAC (when the calculated concentration is within 10% of the steady-state or equilibrium concentration); and, (g) writing the calculated time to achieve the DAC, the DAC concentration, and equilibrium or steady-state concentration to an output data file.

In the revised version of VDRUM1, additional requirements were identified:

1. Program has capability to model VOC transport within a vented waste drum with or without a rigid drum liner and up to four additional layers of confinement;

2. Program has capability to model VOC transport within a vented waste drum that contains layers of confinement that may or may not be vented;

3. Program calculates steady-state concentration using computationally efficient algebraic equations instead of by solving a series of ordinary differential equations.

4. Program has the capability to calculate the time necessary to achieve a specified fraction of the steady-state concentration in the drum headspace or the fraction of the steady-state concentration achieved in the drum headspace for a specified period of time.

4.1 Design Constraints

The computer program for calculating the DAC or the relative VOC concentration in the drum headspace for a given period of time must be able to access the IMSL mathematical library. The IMSL mathematical library contains subroutines specifically designed to solve a series of ordinary differential equations. The computer program and the IMSL subroutines are written in FORTRAN computer language.

4.2 Software Design and Implementation

Major components of the computer code include:

1. All user-specified input data

2. Model parameter definition of gas-specific properties via internal subroutine

3. Model variable initialization

4. An algorithm to calculate steady-state gas concentration within waste drum

5. An algorithm to solve a series of ordinary differential equations of the gas transport model that define the gas concentration within each layer of confinement in the waste drum as a function of time

6. Model results written to an output data file

4.2.1 DAC Calculations

The drum age criterion is defined as the time in which the VOC concentration in the drum headspace achieves 90% of its steady-state concentration. In VDRUM1, the steady-state concentration was determined through the solution of a series of ordinary differential equations to be the concentration at the time it could be considered constant. The steady-state concentration was defined as the concentration when the relative change in concentration was less than 10^{-6} in order to avoid performing calculations out to a time approximating infinity. This approach was an arbitrary way of saying that this condition is close enough to steady-state conditions.

The equations that form the basis for describing transient VOC transport across polymer bags, filter vents, and openings in the drum liner lid as well as model assumptions have been described in earlier software validation documentation.[1] The equations were developed to describe the existence of potentially four layers of confinement – the drum, a liner, a large polymer liner bag, and small polymer bags. The program user was able to specify whether or not small bags were present inside the large liner bag. Only one mechanism for VOC transport across the confinement was assumed in each layer of confinement. There was no capability in the program for the user to specify more than one VOC transport mechanism in a given layer of confinement such as in the case of polymer bags with bag filter vents.

The steady-state concentrations in a waste drum can be efficiently determined algebraically knowing the parameters that affect VOC transport across each layer of confinement. In addition, this approach can account for multiple means of transport across a layer of confinement. In a vented drum, the steady-state rate of VOC transport from the drum can be defined knowing the drum headspace and drum filter vent VOC diffusion characteristic. Also during steady-state conditions, the rates of VOC transport across each layer of confinement are equal. The steady-state concentration in the drum headspace, y_{DH}, can be defined in terms of the VOC transport characteristic across the drum filter vent, D_N^*, the VOC concentration within the innermost layer of confinement, y_1, and the VOC transport characteristics, K_i, across N layers of confinement in an algebraic equation:

$$y_{DH} = y_1[D_N^* \sum_{i=1}^{N} (1/K_i)]^{-1} \qquad (1)$$

If the VOC concentration within the innermost layer of confinement is assumed to remain constant as the result of the surrounding gas phase in equilibrium with the VOC-containing waste, the relative concentration in the drum headspace is defined by rearranging Eqn (1)

$$\frac{y_{DH}}{y_1} = [D_N^* \sum_{i=1}^{N} (1/K_i)]^{-1} \qquad (2)$$

The use of the relative concentration to define the VOC concentration in the drum headspace eliminates the need to know the exact initial concentration within the innermost layer of confinement.

The effective VOC transport characteristic, K_i, across a layer of confinement reflects the combined contributions of VOC diffusion and permeation, and is defined as

$$K_i = K_{p,i} + K_{d,i} + D_i^* \qquad (3)$$

where $K_{p,i}$, $K_{d,i}$, and D_i^* are the VOC permeation, diffusion, and filter vent transport characteristics, respectively, across the i^{th} layer of confinement. In the case where one or more of these transport mechanisms does not occur (i.e., no filter vent present), the corresponding term is set to zero. The units of each term are mol s^{-1}. The units are sometimes alternatively expressed as mol s^{-1} (mol frac)$^{-1}$ reflecting the fact that the product of these terms and the VOC mol fraction difference across a layer of confinement defines the molar rate of VOC transport across the layer of confinement.

The VOC permeation characteristic, $K_{p,i}$, is defined as

$$K_{p,i} = \frac{\Phi A_{p,i} P \rho}{x_{p,i}} \qquad (4)$$

where

Φ	=	4.46e-5 mol cm^{-3}(STP), gas concentration at standard conditions (STP)
$A_{p,i}$	=	permeable surface area of layer of confinement, cm^2
P	=	gas pressure, cm Hg
ρ	=	VOC permeability coefficient, cm^3(STP) cm cm^{-2} s^{-1} (cm Hg)$^{-1}$
$x_{p,i}$	=	thickness of permeable surface area, cm

The VOC diffusion characteristic, $K_{d,i}$, is defined as

$$K_{d,i} = \frac{A_{d,i} D c}{x_{d,i}} \qquad (5)$$

where

$A_{d,i}$	=	opening surface area in confinement layer across which gas diffuses, cm^2
D	=	VOC diffusivity coefficient, cm^2 s^{-1}
c	=	gas concentration, mol cm^{-3}
$x_{d,i}$	=	thickness of permeable surface area, cm

The VOC diffusion characteristic across a filter vent was calculated knowing the VOC-to-hydrogen diffusivity ratio and the hydrogen diffusion characteristic of the filter vent

$$D_i^{*} = \frac{D}{D_{H_2}} D_{H_2}^{*} \tag{6}$$

The diffusivity ratio can be calculated using measured or estimated diffusivity values. In the case where the ratio is estimated using the molecular weight (MW), critical temperature (T_c), and critical pressure (P_c) of hydrogen and the VOC, the ratio is calculated with the following expression:

$$\frac{D}{D_{H_2}} = \frac{(T/298.15)^{1.823}}{P} \left(\frac{P_{c,voc}}{P_{c,H_2}}\right)^{1/3} \left(\frac{T_{c,H_2}}{T_{c,voc}}\right)^{1/2} \left(\frac{\frac{1}{MW_{air}} + \frac{1}{MW_{voc}}}{\frac{1}{MW_{air}} + \frac{1}{MW_{H_2}}}\right)^{1/2} \tag{7}$$

All temperatures are in units of K and pressure is in units of atm.

The DAC is the time required to achieve 90% of the steady-state concentration. The transient behavior of the VOC concentration within a waste drum given a set of initial conditions is modeled by solving a set of differential equations that define the rate of VOC transport across each layer of confinement. The rate of VOC transport across each layer of confinement equals

$$r_i = \frac{\partial(c_i)}{\partial t} = K_i \Delta y_i c \tag{8}$$

where

r_i = rate of VOC across i^{th} layer of confinement

Δy_i = VOC concentration difference across i^{th} layer of confinement, mol fraction

In addition to equations of the form in Eqn (6) for each layer of confinement, VOC solubility in the drum liner is accounted for by the following equation:

$$r_L = \frac{\partial(c_L)}{\partial t} = \eta \Phi V_p P[s_\infty - s] \tag{9}$$

where

r_L = rate of VOC accumulation in the drum liner, mol s^{-1}

c_L = VOC concentration in the drum liner, mol cm^{-3}

η = transfer coefficient, s^{-1}

V_p = volume of drum liner polymer, cm^3 polymer

s_∞ = VOC equilibrium solubility in liner polymer, $[cm^3(STP)\ VOC](cm^{-3}\ polymer)\ (cm\ Hg)^{-1}$

s = average VOC solubility in liner polymer, $[cm^3(STP)\ VOC](cm^{-3}\ polymer)\ (cm\ Hg)^{-1}$

The VOC equilibrium concentration is a function of the volume-average VOC mole fraction in the gas surrounding the liner, y_v

$$s_\infty = \frac{y_v}{H^*} \tag{10}$$

where H^* is the VOC Henrys constant in the drum liner. The transfer coefficient and Henrys constant for each VOC in the polyethylene drum liner was measured experimentally or estimated.[4]

The modified version of VDRUM1 will be referred to as VDRUM2. The VDRUM2 code is listed in Appendix A.

4.2.2 Modification to Data Input File

After specifying the name of the input and output file in the first line (each name in single quotes), the user now specifies the total number of VOCs being considered, the number of layers of confinement, and the number of rigid drum liners (zero or one) in the drum. This tells the code whether or not it needs to consider VOC solubility in the liner. The VOC solubility in all other layers of confinement is considered negligible. For example, the first two lines of an input file may look like

```
'zbase','zbase.out'
12,4,1
```

Two lines of data then follow this information for each VOC. The first line contains the name of each VOC as well as the initial concentration inside each layer of confinement. In the case of newly packaged waste drums, the concentration within the first, or innermost, layer of confinement is set to a nonzero value while the concentration in all other layers are set to zero. The next line specifies the VOC molecular weight, permeability in polyethylene ($cm^3(STP)\ cm\ cm^{-2}\ s^{-1}\ (cm\ Hg)^{-1}$), VOC diffusivity in air at 25°C (if known) ($cm^2\ s^{-1}$) , VOC critical temperature (K), VOC critical pressure (atm), VOC Henrys constant in the drum liner [(cm^3 polymer) atm cm^{-3}(STP) VOC], and VOC mass transfer coefficient (s^{-1}) at the drum liner surface. The known, measured, or estimated values of these parameters for 29 VOCs have been collected.[1,4] An example of VOC input data is listed for toluene

```
'toluene',1000.,0.,0.,0.
92.1,669.e-10,0.0849,594.,41.6,0.002857,7.e-6
```

In code validation and verification, the ratio of VOC-to-hydrogen diffusivity ratio across a filter vent was estimated using the molecular weight, critical temperature, and critical pressure of the VOC.

After all VOC-specific parameters have been specified, the parameters for each layer of confinement are entered beginning with the first layer of confinement. These parameters include (in order) the permeable surface area (cm^2), the diffusion cross-sectional area (cm^2), the total void volume within the layer of confinement (cm^3), the thickness of the permeable surface (cm), the diffusional length (cm), and the hydrogen filter vent diffusion characteristic ($mol\ s^{-1}$). If any of these terms are not applicable for a given layer, they are to be set to zero. Typical data for a layer of confinement consisting of several layers of similar small polymer liner bags are listed below:

14000.,0.,0.,0.038,0.,0.

The parameter values used in the waste drum configurations considered in earlier DAC calculations have been summarized.[1,4] The total permeable area of multiple small bags is estimated to be the total area of all small bags. Values of zero indicate that the parameter is not applicable. Knowledge of the void volume is not required for the first layer of confinement (VOC concentration assumed to be constant). If waste is typically wrapped in multiple layers of bags, the total bag thickness is assumed to be the sum of the bag thicknesses.

Finally, in the last line of the input file, the temperature (°C), pressure (cm Hg), fraction of the drum headspace steady-state concentration to achieve before terminating the code, and the total number of days to calculate the drum headspace concentration are specified. The calculations will stop when one of the two stop criteria are met. If the user wants to determine the DAC to achieve a specific relative concentration, the total number of days should be set to zero. If the user wants to determine the extent of VOC transport in a given time period, the fraction quantity in the last line of the data input file should be set to unity. Both values can be specified if the user wants the code to stop when either one of the criteria is met. In the case of calculating the DAC only at typical conditions, the input file would contain the following information:

25.,76.,0.9,0

If the user wished to determine the relative headspace concentration after 75 days, the input data would read as follows:

25.,76.,1.,75

4.2.3 Validation of DAC Calculations

The validity of the change in the program was determined by comparing the VDRUM2 results predicting the drum age criteria for newly packaged waste drums with results obtained using VDRUM1.[1] A comparison of input and output data files for VDRUM1 and VDRUM2 calculating DAC values for 12 indicator VOCs in identical packaging configurations and packaging scenarios are summarized in Appendix B. The DACs vary by a few days for VOCs that estimated the VOC-to-hydrogen diffusivity ratio using an estimated VOC diffusivity (input files to VDRUM2) instead of value specified by the user (input files to VDRUM1). In the case of toluene, the DAC values calculated using VDRUM1 were 142 and 225 days for the two configurations. The results of VDRUM2 for the same packaging configurations were 142 and 226 days, respectively.

The steady-state concentrations for VOCs that used critical properties to determine the VOC-to-hydrogen diffusivity ratio from VDRUM2 were consistently lower than values calculated in VDRUM1. This is attributed to the change in the calculated VOC diffusion characteristic across the filter vent. For those VOCs where the diffusivity ratio was calculated using the same information, the steady-state concentrations calculated in VDRUM2 were slightly greater than those calculated in VDRUM1. The exact steady-state concentration is calculated in VDRUM2 while an algorithm in VDRUM1 selects a concentration that is not significantly different than the last value calculated. This algorithm inherently will identify a steady-state concentration less than the actual value.

4.2.4 Model Verification

The steady-state concentration for a VOC is calculated using the input parameters specified in the input file and Eqns (2-7). Using input data in ZBASEII for toluene, the following values are calculated:

Layer 1: $K_1 = K_{p,1} = (\Phi\ A_{p,1}\ P\ \rho) / x_{p,1}$
$A_{p,1}$ = 14000 cm^2; P = 76 cm Hg; ρ = 669e-10 cm^3(STP) cm cm^{-2} s^{-1} (cm Hg)$^{-1}$; $x_{p,1}$ = 0.038 cm
$K_{p,1}$= 4.46e-5 (14000) (76) (669e-10)/(0.038) = 8.35e-5 mol/s

Layer 2: $K_2 = K_{p,2} = (\Phi\ A_{p,2}\ P\ \rho) / x_{p,2}$
$A_{p,2}$ = 14000 cm^2; P = 76 cm Hg; ρ = 669e-10 cm^3(STP) cm cm^{-2} s^{-1} (cm Hg)$^{-1}$; $x_{p,2}$ = 0.056 cm
$K_{p,2}$= 4.46e-5 (14000) (76) (669e-10)/(0.056) = 5.67e-5 mol/s

Layer 3: $K_3 = K_{d,3} = (A_{d,3}\ Dc) / x_{d,3}$
$A_{d,3}$ = 0.71 cm^2; D = 0.0849 cm^2 s^{-1}; c = P/RT; P = 76 cm Hg; T=25°C=298 K;
R= 6236 cm^3 (cm Hg) mol^{-1} K^{-1}; $x_{d,3}$ = 1.2 cm
$K_{d,3}$= 0.71 (0.0849) (76/(298)(6236))/1.2 = 2.05e-6 mol/s

Layer 4: $K_4 = D_4^* = (D / D_{H2})\ D_{H2}^*$

$$\frac{D}{D_{H_2}} = \frac{(T/298.15)^{1.823}}{P}\left(\frac{P_{c,voc}}{P_{c,H_2}}\right)^{1/3}\left(\frac{T_{c,H_2}}{T_{c,voc}}\right)^{1/2}\left(\frac{\dfrac{1}{MW_{air}}+\dfrac{1}{MW_{voc}}}{\dfrac{1}{MW_{air}}+\dfrac{1}{MW_{H_2}}}\right)^{1/2}$$

T = 298.15 K; P = 1 atm; $P_{c,voc}$ = 41.6 atm; P_{c,H_2} = 12.8 atm; T_{c,H_2} = 33.3 K; $T_{c,voc}$ = 594 K; MW_{air} = 29; MW_{voc} = 92.1; MW_{H_2} = 2.016; D_{H2}^*= 42.e-7 mol/s

$$\frac{D}{D_{H_2}} = (1)(41.6/12.8)^{0.3333}\ (33.3/594)^{0.5}\ [(1/29+1/92.1)/(1/29+1/2.016)]^{0.5} = 0.1025$$

K_4=(0.1025)(42.e-7) = 4.30e-7 mol/s

$$\frac{y_{DH}}{y_1} = [4.3\text{e-}7(1.20\text{e}4 + 1.76\text{e}4 + 4.88\text{e}5 + 2.33\text{e}6)]^{-1} = 0.8180$$

Given y_1 = 1000 ppmv, y_{DH} = 818.0 ppmv.

From ZBASEII.OUT, the steady-state concentration for toluene = 818.0 ppmv

4.2.5 System Limitations

The primary system limitation is the requirement that the computer code has access to an IMSL mathematical library containing the called subroutine, written in FORTRAN, designed to solve a series of ordinary differential equations. Currently, a Visual FORTRAN compiler with an IMSL mathematical library is used to compile the computer code. In the past, as a result of hardware upgrades, previous FORTRAN compilers became obsolete. This required that a new FORTRAN compiler be acquired. There is always a risk that the current FORTRAN compiler may become incompatible with future computer hardware. It is the responsibility of the user and maintenance support to insure that this situation is avoided.

4.2.6 Anticipated Errors

No computational errors are anticipated.

4.2.7 User and Maintenance Support

As of June 30, 2000, user and maintenance support of the computer code is provided by Andrea Chambers at the Idaho National Engineering and Environmental, Idaho Falls, Idaho. A copy of the computer codes as well as a record log will be maintained to record any code updates. If the software is significantly changed, baseline validation will be performed to determine if there is any significant or undesirable impact on software input.

5. REFERENCES

1. K.J. Liekhus, 1995, "Validation of gas transport modeling computer codes", INEL-95/121, Idaho National Engineering Laboratory, Idaho Falls, ID.

2. *Safety Analysis Report for the TRUPACT-II Shipping Package*, 1999, Rev. 18, Westinghouse Electric Corporation, Waste Isolation Division, Carlsbad, NM.

3. *Handbook of Chemistry and Physics*, 59th ed., 1979, CRC Press, Boca Raton, FL.

4. M.J. Connolly et al., 1998, *Position for Determining Gas Phase Volatile Organic Compound Concentrations in Transuranic Waste Containers*, INEEL-95/0109, Rev. 2, LMITCO, Idaho Falls, ID.

Appendix A

Appendix A

```
c**************************************************************************
c************ VDRUM2.FOR = "VDRUM.FOR (Rev. 2)" *************************
c
c Original program written by: Kevin J. Liekhus
c                    Lockheed Idaho Technologies, Co.
c                    Idaho National Engineering Laboratory
c Date: April 26, 1995
c**************************************************************************
c*** Modified: 06/15/2000
c*** Modifications:
c  1) Program now calculates time to achieve percentage of steady-state
c     concentration in drum with or without drum liner, with up to
c     four (4) other layers of confinement through which VOCs may
c     permeate the surface (polymer bag), diffuse across an opening,
c     or diffuse across a filter vent.
c  2) Option to calculate percentage of steady-state concentration after
c     specified number of days.
c  3) Steady concentration is calculated directly based on the
c     waste drum configuration
c  4) Eliminate cases where gas generation is considered
c  5) Eliminate case of newly packaged, unvented drum/liner
c**************************************************************************

c----- Model of gas transport in vented and unvented waste drums
c----- calculates time when gas concentration in drum headspace is within
c----- x% of the steady-state gas concentration. (Variable x defined by user)
c
c----- This program is written in FORTRAN and utilizes an IMSL FORTRAN
c----- subroutines for mathematical applications. The IMSL subroutine (IVPAG)
c----- solves a series of first-order ordinary differential equations.
c
c----- MODEL ASSUMPTIONS AND IMPORTANT FEATURES ---------------------
c----- : Ideal gas behavior
c----- : Constant temperature in waste drum
c----- : Gas concentration throughout a void volume is uniform at all times
c----- : Drum configuration: waste drum, rigid drum liner (optional),
c-----    and one to four additional layers of confinement
c----- : In case of multiple layers of bags (of same size), treat as one
c-----    bag with thickness equal to sum individual bag thicknesses
c----- : In case of multiple layers of bags, each with a filter vent,
c-----    define a single-bag filter vent diffusion characteristic = D*/n
c-----    (filter vent diffusion char. divided by the number of bags)
c----- : In all layers of confinement (excluding drum liner and drum)
c-----     Permeation of the gas, diffusion of gas across an opening,
c-----     and diffusion of gas across filter vent are modeled.
c----- : In the case of multiple innermost layers of confinement
c-----    (i.e., many small bags containing waste), the innermost layer
c-----    of confinement is treated as a single volume with a surface area
```

```
c-----   and filter diffusion characteristic equal to the sum of these
c-----   values from the individual packages.
c----- : In drum liner, gas diffuses across opening or filter vent in
c-----    drum liner lid.
c----- : Diffusion of gas across drum filter vent is primary means
c-----    of transport out of the drum
c----- : All filter vents are characterized by hydrogen
c-----    diffusion characteristic (mol/s)
c----- : Gas/vapor solubility in drum liner characterized by
c-----    Henry's constant
c----- : Gas/vapor solubility in drum liner is assumed to be a linear
c-----    function of the volume-averaged VOC gas-phase concentration
c-----    between drum liner void volume and void volume outside the liner
c----- : Dissolved gas concentration in drum liner is uniform
c-----    (not necessarily constant) at all times
c----- : All model parameter inputs remain constant.
c----- : Gear's backward difference method used to solve series of
c-----    ordinary differential equations
c----- : Initial conditions
c-----    - Gas concentrations within each void volume (specified by user)
c-----    - Dissolved gas concentration in drum liner is initially defined
c-----      in terms of the initial gas concentration in drum liner headspace
c----- : Boundary conditions
c-----    1) VOC concentration, outside drum filter vent = 0
c-----    2) VOC concentration, innermost layer of confinement = constant

c***********************************************************************
c********************* MAIN PROGRAM *************************************
c***********************************************************************

      character*32 test,ifname,ofname,vocid(35)
      real aa(1,1),yy(35,7),yz(7),y(7),k
      real pm(35),df(35),amw(35),tc(35),pc(35),h(35),ak(35)
      real param(50),ap(7),ad(7),v(7),xp(7),xd(7),dfh(7)
      integer ivoc(35)
      common/qq/p,d,ap,ad,v,xp,xd,dfh,dfr,pHg,temp0,c0,s0,k,nlin
      external fcn,ivpag,sset
c***********************************************************************
c***** USER-SUPPLIED INPUT **********************************************
c***********************************************************************
c-------------------------------
c specify input data file name
c-------------------------------
      write(*,9)
    9 format(1x,'Enter name of input data file  ')
      read(*,*)ifname
      open(unit=3,file=ifname,status='unknown')

c-----------------------------
c reading of input data file
c-----------------------------
```

```
c----- User provided input
c-----   test - text or title describing contents of input data file
c-----   ofname - output file name
c-----   ncom - number of compounds in gas phase of innermost layer
c-----   nlay - total number of layers of confinement
c-----   nlin - total number of drum liners in waste drum (0 or 1)
c-----   vocid - name of gas or VOC
c-----   yy(i,n) - i-th VOC concentration (ppmv) in n-th layer of confinement
c-----        n=1, headspace within innermost layer of confinement
c-----        subsequent layers of confinement are numbered 2, 3, etc.
c-----   amw(i) - gas/VOC molecular weight
c-----   pm(i) -  gas/VOC permeability coefficient in polymer bag,
c-----            cm3(STP) cm/(cm2 s cm Hg)
c-----   df(i) -  gas/VOC diffusivity in air, cm2/s
c-----   tc(i) -  critical temperature of gas or VOC, K
c-----   pc(i) -  critical pressure of gas or VOC, atm
c-----   h(i) -   gas/VOC Henry's constant for drum liner,
c-----            cm3 polymer atm/cm3 (STP) gas
c-----   ak(i) -  gas/VOC mass transfer coefficient at drum liner surface, 1/s
c-----   ap(n) - total permeable surface area (cm2) of n-th layer of confinement
c-----   ad(n) - cross-sectional area of opening (cm2) across n-th layer
c-----   v(n) - void volume within n-th layer of confinement (cm3)
c-----   xp(n) - permeable surface thickness (cm) of n-th layer
c-----   xd(n) - diffusional path length (cm) across n-th layer of confinement
c-----   dfh(n) - vent hydrogen diffusion characteristic of n-layer, mol/s
c-----   temp - drum temperature, C
c-----   pHg - atmospheric pressure, cm Hg
c-----   yssfrac - fraction of drum headspace steady-state concentration,
c-----      for which the time required to reach this fraction is calculated
c-----      if program ends after simulating (nday) days, set yssfrac=1.0
c-----   nday - number of days over which to calculate model results,
c-----      if want to calculate to specific value of yssfrac, set nday=0
c
      read(3,*)test,ofname
      read(3,*)ncom,nlay,nlin
      do 8 i=1,ncom
        read(3,*)vocid(i),(yy(i,j),j=1,nlay)
        read(3,*)amw(i),pm(i),df(i),tc(i),pc(i),h(i),ak(i)
  8   continue
      read(3,*)(ap(j),ad(j),v(j),xp(j),xd(j),dfh(j),j=1,nlay)
      read(3,*)temp,pHg,yssfrac,nday
c***********************************************************************
c***** INITIALIZATIONS AND CONVERSIONS *********************************
c***********************************************************************
c-----   r0 - gas constant (82.06 cm3 atm/mol K)
c-----   patm - atmospheric pressure, atm
c-----   temp0 - initial drum temperature, K
c-----   c0 - initial ideal gas concentration in drum, mol/cm3
      r0=82.06
      patm=pHg/76.0
      temp0=temp+273.15
```

```
      c0=patm/(r0*temp0)
c---------------------------
c opening of output data file
c---------------------------
      open(unit=2,file=ofname,status='unknown')
      write(2,15)test
 15   format(1x,a32)
c---------------------------
c write header to output file
c---------------------------
      write(2,143)
 143  format(27x,'N(days)',2x,'[]@N',4x,'[]@SS',3x,'0.9[]SS/[]N')
c-------------------------------------------------------
c calculate i-th compound concentrations throughout waste drum
c-------------------------------------------------------
      do 43 i=1,ncom
c calculate diffusion properties for VOC/gas
c*****************************************************************
        CALL VPROP(amw(i),tc(i),pc(i),df(i),dfr,c0,h(i),s0,temp0,patm)
c*****************************************************************
c----- calculate steady-state concentration for i-th compound
        sumi=0
        do 33 j=1,(nlay-nlin)-1
          a=0.
          b=0.
          if(ap(j).ne.0.)a=4.46e-5*pm(i)*ap(j)*pHg/xp(j)
          if(ad(j).ne.0.)b=(df(i)*ad(j)/xd(j))*c0
          sum=a+b+dfr*dfh(j)
          sumi=sumi+1./sum
 33     continue
        if(nlin.eq.1)then
         blin=(df(i)*ad(nlay-1)/xd(nlay-1))*c0+dfr*dfh(nlay-1)
         sumi=sumi+1./blin
        end if
        dvent=dfr*dfh(nlay)
        sumi=sumi+1./dvent
        yss=yy(i,1)/(dvent*sumi)
c-----------------------------------------------------------------
c  calculate drum headspace gas concentration as a function of time
c-----------------------------------------------------------------
c----- IMSL subroutines and parameters
c-----  SSET - IMSL subroutine (sets a vector to a constant value)
c-----  IVPAG - IMSL subroutine (initial-value ODE solver)
c-----   ido - flag indicating state of computation
c-----   a(1,1) - matrix used when ODE system is implicit
c-----   tend - value of t at which solution is desired
c-----   tol - tolerance for error control
c-----   param - vector of length 50 containing optional parameters,
c-----         model parameters set to default values
c-----    param(4) - maximum number of steps allowed
c-----    param(10) - switch determining error norm
```

```
c-----     param(12) - method indicator
c-----        1 = Adams' method;
c-----        2 = Gear's backward difference method
c initialize IMSL parameters, set param to default values
      mxparm=50
      CALL SSET(mxparm,0.0,param,1)
      param(4)=10000000
      param(10)=2
      param(12)=2
      ido=1
      tol=1.e-6
c----- initialization of other variables
c-----  yz(n) - VOC concentration in n-th layer of confinement, mol/cm3
c-----  yz(nlay+1) - VOC concentration in drum liner, cm3 VOC/cm3 polymer
c-----  y(n) - VOC concentration in n-th layer of confinement, ppm
c-----  t - time (sec)
c-----  nc - number of days simulated in program
c-----  ndac - time to achieve fixed percentage of steady-state conc.
c-----  yss - steady-state gaseous compound conc. in outermost layer
c-----  rr - DAC concentration, ppm
c-----  zneq - VOC concentration in outermost layer on (nc-1)th day
c-----  p -  gas/VOC permeability coefficient in polymer bag,
c-----          cm3(STP) cm/(cm2 s cm Hg)
c-----  d -  gas/VOC diffusivity in air, cm2/s
c-----  dvent -  gas/VOC diffusion characteristic across drum filter vent,
c-----          mol/s(/fraction)
c-----  k -  gas/VOC mass transfer coefficient at drum liner surface, 1/s
c-----  fcn - user-supplied subroutine to evaluate functions
c-----  fcnj - user-supplied subroutine to compute the Jacobian
      t=0.
      nc=1
      nq=nlay+nlin
c convert gas concentration from ppmv to mol/cm3
      do 37 j=1,nlay
        yz(j)=yy(i,j)*c0*1.e-6
  37  continue
c
c----- VPROPS - subroutine calculate VOC properties not specified
c-----  df - VOC diffusivity in air, cm2/s
c-----  difr - ratio of VOC-to hydrogen diffusivity
c-----  s0 - gas pressure/(total gas concentration*VOC Henry's constant),
c-----        [(cm3 VOC(STP)/(cm3 polymer)]/(mol/cm3)
c******************************************************************
      CALL VPROP(amw(i),tc(i),pc(i),df(i),dfr,c0,h(i),s0,temp0,patm)
c******************************************************************
      if(nlin.eq.1)yz(nlay+1)=yz(nlay-1)*s0
      p=pm(i)
      d=df(i)
      k=ak(i)
```

```
c*********************************************************************
c***** MODEL CALCULATIONS ********************************************
c*********************************************************************
 20    if(p.gt.50.e-10)then
c-----  dt - time interval (sec)
        dt=120.*50.e-10/p
        if(dt.lt.12.)dt=12.
      else
        dt=120.*5.e-10/p
      end if
c-----  tend - total time (sec)
      tend=t+dt
c
      CALL IVPAG(ido,nq,fcn,fcnj,aa,t,tend,tol,param,yz)
c
c*********************************************************************
c***** MODEL OUTPUT **************************************************
c*********************************************************************
c-------------------------------
c output (every simulated 24 hrs)
c-------------------------------
      if(ifix((tend+0.1)/86400).eq.nc)then
       y(nlay)=(yz(nlay)/c0)*1.e6
c test if concentration or time quit criteria are met
       if((y(nlay).gt.yssfrac*yss).or.(nc.eq.nday))then
        ndac=nc
        rr=y(nlay)
       else
        nc=nc+1
        goto 20
       end if
      else
       goto  20
      end if
c------------------------------------------
c write to output data file
c------------------------------------------
      write(2,34)vocid(i),ndac,rr,yss,(0.9*yss)/rr
 34    format(1x,a25,2x,i4,2x,f7.2,2x,f7.2,5x,f5.1)
c------------------------------------------
c NOTE:
c Ratio [(0.9*yss)/rr] equals [VOC conc.@ndac/VOC conc.@90%ofSS]
c Thus, if DAC was determined at 90% of SS,  ratio = 1.0
c-------------------------------
c final call to release workspace
c-------------------------------
      ido=3
      CALL IVPAG(ido,nq,fcn,fcnj,aa,t,tend,tol,param,yz)
  43 continue
     end
```

```
      SUBROUTINE FCN(neq,t,y,yp)
      real y(neq),yp(neq),p,d,ap(7),ad(7),v(7),xp(7),xd(7),dfh(7),k
      common/qq/p,d,ap,ad,v,xp,xd,dfh,dfr,pHg,temp0,c0,s0,k,nlin

c-------------------------------------------------------------------
c----- MODEL EQUATION ASSUMPTIONS
c----- : VOC concentration within innermost layer of confinement remains
c-----   constant; therefore yp(1)=0
c----- : VOC equilibrium concentration in drum liner is defined in terms
c-----   of a volume-average VOC concentration in the void volumes
c-----   (drum liner and drum headspaces) surrounding the drum liner
c-------------------------------------------------------------------
c-----  neq - number of ordinary differential equations
c-----  t - independent variable, time (s)
c-----  y(i) - dependent variable: (i=1,neq-1) = gas VOC concentration (mol/cm3)
c-----     (i = neq) VOC concentration in polymer (cm3 VOC/cm3 polymer)
c-----  yp - first derivative of y with respect to t
c-----  a = 4.46e-5*p*ap(i)*pHg/xp(i), mol/s
c-----  b = c0*d*ad(i)/xd(i), mol/s
c-----  dvent = dfr*dfh(i), mol/s
c-----  q - rate of VOC transport from layer of confinement, mol/s
c-----  g4 - fraction of VOC in drum liner headspace of all VOC in both
c-----      drum liner and drum headspaces
c-----  g5 = 1 - g4
c-----  vp - volume of polymer in drum liner, cm3
c-----  s - VOC equilibrium concentration in drum liner as defined in terms
c-----     of volume-average VOC concentration surrounding drum liner, cm3 VOC/cm3
c-----  s0 - VOC equilibrium concentration in drum liner as defined in terms
c-----     of VOC vapor pressure in saturated vapor, cm3 VOC/cm3
c-----  stp - gas concentration (mol/cm3) at standard temperature (273.15 K)
c-----       and pressure (1 atm) = 1./(82.06*273.15) = 4.461e-5 mol/cm3
c-----  dvent - VOC diffusion characteristic, mol/s
c-----  k - VOC mass-transfer coefficient, 1/s
c----------------------------------------------------------
c----- i-th layer of confinement (excluding drum liner, drum)
c----------------------------------------------------------
      q=0.
      nj=neq-2*nlin-1
      do 53 j=1,nj
        a=0.
        b=0.
        if(ap(j).ne.0.)a=4.46e-5*p*ap(j)*pHg/xp(j)
        if(ad(j).ne.0.)b=(d*ad(j)/xd(j))*c0
        dvent=dfr*dfh(j)
        sum=a+b+dvent
        yp(j)=(-q+sum*(y(j+1)-y(j))/c0)/v(j)
        yp(1)=0.
        q=sum*(y(j+1)-y(j))/c0
 53   continue
c----------------------------------------------------------
c drum liner headspace with punctured/vented liner lid (nlin=1)
```

```
c-----------------------------------------------------------------
     if(nlin.eq.1)then
c--------------------------------
c be sure liner headspace concentration > 0
c--------------------------------
      if(y(nj+1).gt.1.e-12)then
       g4=y(nj+1)*v(nj+1)/(y(nj+1)*v(nj+1)+y(nj+2)*v(nj+2))
       g5=1-g4
       vp=ap(nj+1)*xp(nj+1)
       s=s0*(y(nj+1)*v(nj+1)+y(nj+2)*v(nj+2))/(v(nj+1)+v(nj+2))
      else
       s=0.
       g4=0.
       g5=0.
      end if
      b=c0*d*ad(nj+1)/xd(nj+1)
      dvent=dfh(nj+1)*dfr
      sum=b+dvent
      stp=1./(82.06*273.)
      vs=g4*vp*stp
      yp(nj+1)=(-q+sum*(y(nj+2)-y(nj+1))/c0-vs*yp(nj+3))/v(nj+1)
      q=sum*(y(nj+2)-y(nj+1))/c0
c---------------------
c------ drum headspace
c---------------------
      dvent=dfr*dfh(nj+2)
      yp(nj+2)=(-q-dvent*y(nj+2)/c0-g5*yp(nj+3)*vp*stp)/v(nj+2)
c------------------------------
c------ polyethylene drum liner
c------------------------------
      yp(nj+3)=k*(s-y(nj+3))
     else
c---------------------
c------ drum headspace (no liner)
c---------------------
      dvent=dfr*dfh(nj+1)
      yp(nj+1)=(-q-dvent*y(nj+1)/c0)/v(nj+1)
     end if
c
     return
     end

     SUBROUTINE FCNJ(neq,t,y,dypdy)
     real y(neq),dypdy(*)
     return
     end
```

```
      SUBROUTINE VPROP(amw,tc,pc,df,dfr,c0,h,s0,t,pr)
c--------------------------------------------------------------------------
c-----   amw - gas molecular weight
c-----   tc - critical temperature (K) of gas
c-----   pc - critical pressure (atm) of gas
c-----   df - gas diffusivity in air (at 25 C if temperature not specified)
c-----   dfr - ratio of gas/Hydrogen diffusion coefficients
c-----   h - gas Henry's constant, cm-3 gas (STP) cm3 polymer (atm)
c-----   s0 - gas pressure/(gas Henry's constant * total gas concentration)
c-----          (cm3 gas/cm3 poly)(cm3 gas/mol gas)
c-----   pch - critical pressure (atm) of hydrogen
c-----   tch - critical temperature (K) of hydrogen
c-----   pca - critical pressure (atm) of air
c-----   tca - critical temperature (K) of air
c-----   h2mw - molecular weight of hydrogen
c-----   airmw - molecular weight of air
c-----   smw = 1/airmw + 1/h2mw = 0.5305
c-----   pt - P, T correction relative to 1 atm, 298.15K (25C)
c
      pch=12.8
      tch=33.3
      pca=36.4
      tca=132.
      h2mw=2.016
      airmw=29.
c--------------------------------------------------------------
      if(df.eq.0)then
       if(tc.ne.0.)then
        smw=1./airmw+1/h2mw
        samw=sqrt(1./airmw+1/amw)
        sqmw=samw/sqrt(smw)
        df=2.745e-4*(t**1.823/pr)*(pc*pca)**(1./3.)*samw/sqrt(tca*tc)
       end if
      end if
c
      smw=1./airmw+1/h2mw
      samw=sqrt(1./airmw+1/amw)
      sqmw=samw/sqrt(smw)
      pt=(1./pr)*(t/298.15)**1.823
      dfr=pt*((pc/pch)**(1./3.)*(tc/tch)**(-0.5)*sqmw)
c
      if(h.ne.0.)then
       s0=pr/(c0*h)
      else
       s0=0.
      end if
c
      return
      end
```